RESEARCHES ON CELLULOSE

II

(1900–1905)

BY

CROSS & BEVAN

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CELLULOSE

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PREFACE

Chemists of previous generations have paid relatively little attention to the amorphous or colloidal state of matter; and the appearance of uncrystallisable products of reaction, in investigations of carbon compounds, usually evoked the epithet of 'Schmiere,' applied rather as an epitaph. This procedure was perhaps the expression of a constitutional preference for bodies of certain typical physical characteristics, but actually we think it implied the recognition, partly reasoned, partly instinctive, that in the colloidal state we lose touch of the organic relationships which obtain in the great groups of carbon compounds defined and represented by constitutional formulæ.

If cellulose had been thus met with as an amorphous product of reaction—that is, in its alternative structureless forms—it might very well have been included in the heterogeneous class of 'Schmier' compounds; it certainly would not have attracted the attention of investigators to the degree of devotion of which it has been the object. It might be held that the attractiveness of 'cellulose' as a subject of investigation lies in considerations of utility, and that only its disproportionate technical importance could have supplied the motive for researches which lack the clear direction and control of the leading antecedent generalisations of the science. Obviously, on the other hand, the prominence of cellulose in the arts is the

correlative of its position in the 'natural' world; and this, its prominence in the natural order, is the basis of its attractiveness to us as students of natural philosophy.

The purpose of this volume is to record the recent advances made in our knowledge of the subject-matter, but more expressly to apply the results to the clearing of the issues contained in the question, 'What is cellulose?' The investigations of chemists through two generations have contributed a large amount of exact knowledge of the subject-matter, but the central question is unanswered, and there are very few attempts at its solution.

During the period 1900–05 there have appeared some valuable contributions to the science of the subject, the more important of which we have reviewed in this work. We have ventured to add some critical notes, which we hope will rank as a criticism of appreciation: the intention being to point the particular contributions to the issues contained in the central question, on which the authors themselves are, for the most part, silent.

Our main purpose is to establish, at a juncture which we consider to be critical, as it is favourable to progress, the definitely agnostic position, which involves the recognition of current views of the constitution of cellulose as inadequate, reopens the matter from a more comprehensive point of view, and reduces all or any interpretations of the experimental quantitative facts to their present actual level of 'theoretical' anticipations of final generalisations. In the next place we desire to state the grounds for a considerable widening of the scope of the investigations which will be necessary for reaching such final generalisations of inclusive and exclusive value. There have been many attempts to solve the problem of the constitution of cellulose in terms of molecular formulæ. These essays postulate 'molecules' as the ultimate reacting units of

cellulose, and generally extend the analogies of the 'molecular state' to bodies of this class without, we think, sufficient inquiry as to whether such methods of interpretation are really adequate. There are valid grounds for a considerable modification of these methods of interpretation and an extension of the experimental investigations, in order to pass from a sphere of discussion which is rather academic than real, into a more direct and comprehensive attack of the fundamental problem, 'What is cellulose?'

In dealing with the subject from this point of view, we certainly put scientific before industrial developments, at the same time recognising that these terms rather lose their significance in a region where the industrial developments are entirely scientific in character, and 'theoretical science' has not suggested any positive directions of progressive investigations. From the present, however, we consider that the lines of industrial progress will be rather directed by the application of general theory than the pursuit of technical objectives, and we have endeavoured to illustrate this conclusion in the indications of investigations which are urgently needed for the immediate solution of technical problems, and ultimately as a contribution to the solution of the central problem.

We are indebted to our friend Prof. Sir William Ramsay for important suggestions, and we also wish to recognise the valuable assistance of our collaborator, Mr. J. F. Briggs, in the production of this work.

4 New Court,
London, W.C.

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RESEARCHES ON CELLULOSE

II

SECTION I

CHAPTER I

CELLULOSE AS A TYPICAL COLLOID

IN our previous treatises and special publications we have of necessity written under the influence of the dominant idea or aim of the science, which in relation to cellulose would imply that its reactions and chemical history should find expression in a constitutional formula—a formula sufficiently exact to define its relationship to the great mass of carbon compounds, in the order and arrangement constituting the imposing fabric of 'organic' chemistry, and sufficiently comprehensive to include and set out its various re-activities. But at the same time we have been aware that this assumption is a pre-judgment, if not a prejudice; and in view of the insufficiency of the evidence in relation thereto, it was necessary to adopt the more 'evolutionary' plan of methodically recording the experimental facts, without reference to anything beyond the logic of the method. The basis of the method was an arrangement of the experimental matter on the broadest lines of classification, namely:

1. Reactions of synthesis.

2. Reactions of decomposition, chiefly hydrolysis, acid and alkaline, and oxidation.

To study and set out the empirical facts in relation to the prototype of the group—viz. cotton cellulose—was the necessary preliminary to dealing with the entire group. To differentiate and classify the members of the group, we could only take advantage of reactions of decomposition. The celluloses, as a group, have a close general resemblance to the prototype in giving synthetical derivatives of similar character and composition; but in relation to hydrolysis and the products of decomposition there are divergences sufficiently wide to constitute a positive basis of classification; notably (1) resistance to hydrolytic agencies, and (2) the proportion of furfural obtained by decomposition with condensing acids. Lastly, the celluloses occur in the natural world not in the pure state, but combined or mixed with groups of divergent character. On these broad lines of difference we are enabled to classify as chemical individuals these structural components of vegetable tissues, and they present three well-marked groups—the pecto-celluloses, ligno-celluloses, and cuto-celluloses.

Now, from the point of view of systematic chemistry, it might be urged that this diversified group of compounds can or must be treated independently of all other considerations than those appertaining to matter as matter. Questions of visible structure, questions of physiological function, are irrelevant. It is self-evident that each of the great groups of carbon compounds has innumerable points of contact with the natural world, and that there is a 'natural history' of carbon compounds which complements their systematic interior relationships. But it is true, and perhaps remarkably true, that the latter have entirely excluded the former in the

evolution of the science; and more than this, that considerations drawn from the vital origin and relationships of 'organic' compounds have proved rather an impediment than an aid to progress. This aspect of the science has been exhaustively dealt with in the recently published and admirable treatise of Meldola's on 'The Synthesis of Vital Products,' and it would be superfluous on our part to re-argue the theme. 'Organic chemistry' is itself a structure, of independent and self-contained existence, of which 'life' is an exterior incident and without modifying influence, so far as we can see, on its fundamental basis—that is, on the properties of matter as matter.

But while we accept this substantial conclusion in its latest presentment, we may be permitted to draw issue with the author on the form in which it is presented, since this has an immediate bearing on our subject. The form of the author's 'argument' is indicated by the title of the work, 'The Synthesis of Vital Products.' But the products dealt with are not 'vital.' They are strictly 'by-products' of vital actions or processes, and these are immediately purely chemical in character. There is an implication in the title that 'chemical' synthesis—i.e. laboratory methods of production—may be extended to products which are, in the strict sense of the term, vital. While we do not contend that the proposition is unthinkable, we hold that its introduction, even by suggestion, into the sphere of the practical politics of the science, tends rather to shelve and obscure problems which are now presented to us for investigation. These problems concern the relations of organic form or structure to chemical composition, which, in the case of the cellulose group, are evidently very intimate. It would, of course, be possible to ignore this correlation, and to write a treatise on cellulose in which the various members of the group are dealt with as chemical

individuals purely, and all questions of form or structure merged into their common description as amorphous or colloidal aggregates.

We suggest that this would be an arbitrary procedure, if only in view of *à priori* considerations, notably: First, that the celluloses and allied compounds are formed exclusively as the products of vital processes, of which they are, in turn, the arena; secondly, they are produced in specialised mass-forms; thirdly, their formation postulates a condition of matter in which the molecular energies are dominated by a physical *force majeure* the effects of which persist in the underlying ultimate or chemical configuration of the aggregate. On this view, visible and external structure is intimately correlated with the ultimate configuration of the chemical units: becomes a positive subject of investigation.

But on *à posteriori* grounds the special study of the celluloses compels the inclusion in the area of investigation of all questions relating to external form. As in many other developments of the science, industrial applications have preceded scientific investigation, and the newer industrial uses of the celluloses are largely conditioned by the facts:

1. That the structural features of the celluloses persist in many of their derivative compounds.

2. That the solutions of these derivative compounds are plastic, and are employed in producing artificially moulded solids in continuous masses and any required dimensions, fibres, films, and massive aggregates.

It is an obvious consequence that the more 'progressive' researches with which we shall have to deal in this work are intimately bound up with questions of external form or structure. We do not wish to imply that there is any immediate significance to us in any particular form in which the natural celluloses are produced, nor that the artificially pro-

duced solids are to be regarded as structures in the same sense. They are rather internally homogeneous and structureless; solidified in continuous mass, with any required external form and dimensions. But it is none the less true that the physical properties of these artificial forms are definitely related to the structural qualities of the original cellulose, and these again are shown to be definitely related to chemical constitution.

We may sum up the argument in the statement, which we shall have occasion to elaborate at a later stage, that cellulose is *essentially an aggregate*; the nature of this aggregate is a present definite object of investigation. It is by no means necessary that our ideas of discrete constituent molecular units apply to aggregates of this class. It is, as we know, generally stated that cellulose is a complex polymeride of a unit molecule of dimensions C_6, and of the general type of the carbohydrates, aldose or ketose. As a matter of fact, this view has not contributed to the progress of research; and its vagueness is seen in the necessity for continually altering the dimensions of the supposed polymeride. Thus, in the case of the nitric esters, which have been more extensively investigated than any other group of derivatives, it has been found necessary to abandon the C_{12} formula (Eder) in favour of the C_{24} formula (Vieille), in order to avoid the formulation of nitrates representing fractional proportions of the assumed ultimate C_6. And later researches (p. 30) invalidate the assumption that the arbitrarily enlarged unit has any final value.

If we could assign any final value to the experimental numbers obtainable in this and other series of derivatives, we should be justified in the assertion that cellulose is an aggregate of *essentially* variable dimensions. This hypothesis is unavoidable as an alternative to be critically examined.

It is of course evident that cellulose is a representative

colloid, and therefore that the investigation of the colloidal state generally, which of late years has taken very definite shape, will have furnished some conclusions available for our special case. We cannot attempt here any exhaustive notice of the recent extensive literature of the subject, and, without preface, we proceed to apply a critical statement contained in a dissertation, 'Neue Gesichtspunkte zur Theorie der Kolloide,' by E. Jordis.[1] This author says (p. 63): 'In opposition to prevailing opinion I regard the colloids, and more particularly the hydrosols, not as pure forms of matter, but as the analogues of chemical compounds in dilute aqueous solution . . . formed as the products of a normal dissociation and hydrolysis of crystalloids in aqueous solution.'

This conclusion follows from an examination of the essential conditions presented by typical inorganic colloids, viz. (1) These colloids are, in the main, compounds of polyvalent elements; hence they break up by dissociation (hydrolysis) into mixtures of ions of maximum complexity. (2) This complexity is particularly determined by the amphoteric functions of the hydroxides. (3) The limiting equilibrium as between hydrosol and hydrogel is a definite saline equilibrium or neutral point. Thus in the case of sodium silicate the neutral point is reached with the ratio $Na_2O.30SiO_2$; and the hydrosol which results from treating the silicate with excess of HCl may be formulated as a species of chloride $[Si(OH)_4]_n.Si{<}^{(OH)_3}_{Cl}$; one of the OH groups of the hydroxide having a basic function.

Similarly in the case of ferric hydrate, the neutral point is formulated as $[Fe(OH)_3]_n.Fe{<}^{(OH)_2}_{Cl}$; and the hydrosol is stable up to the limiting ratio 1Cl : 10Fe. In the presence of

[1] Erlangen, February 23, 1904.

organic acids, &c., stable alkaline hydrosols are formed, the (OH) groups of the hydroxide assuming an acid character. These two cases are cited as types. Similar conclusions have been arrived at independently in regard to cellulose. In describing experiments which demonstrated a specific electrical conductivity of cellulose in presence of water, together with electrolytic reactions observed in a circuit completed by moistened cellulose, we used the expression 'It is another link in the chain of demonstration of those characteristics . . . which, for want of a better term, we describe as "saline"' (J. Chem. Soc. 1895, p. 451).

In previous works we have pointed out that the actions of solvents of cellulose can only be explained as the result of its amphoteric activity; that the solution of cellulose in zinc chloride and cuprammonium solutions are to be regarded as containing a species of colloidal double salt.

These considerations result in a working hypothesis which may be briefly formulated as follows: Cellulose does not react as a polymeride of pre-formed hexose groups of rigid configuration, but as a labile complex of groups of varying dimensions representing a state of matter somewhat analogous to that of a solution of a saline electrolyte—that is, it reacts rather as a solution-aggregate than by a succession of molecular combinations; the masses actually reacting following the stoichiometrical ratios proper to the dimensions of these ultimate groups, and retaining their relationship in the aggregate, which is thus progressively modified by the entrance of the new groups.

This view, implying a species of continuous reactivity, may appear at first sight to conflict with current teaching; but on further examination it will be found that the paradox on the surface involves no antagonism in essential principle. We may still regard cellulose as substantially a polymeride of

hexose groups, but modifying our view of such an aggregate as of invariable function and fixed dimensions. We take the constituent molecules as so related that when reaction takes place, more especially under conditions which involve the presence of hydroxyl or of hydrogen ions, the effect of reaction upon a particular molecular unit are communicated to other units, which are consequently modified in function, becoming more or less basic or acidic; hence a complex reacting unit of variable or changing function. It is also necessary to assume that cellulose is ionised both as acid and base, and is then amphoteric. We have thus at once (*a*) an acid, (*b*) a base—that is, hydrogen and hydroxyl ions, and the corresponding complex residual groups—and (*c*) non-ionised molecules, susceptible of similar transformations, with the changing conditions of equilibrium; hence a reacting unit of variable dimensions. Lastly, the exceptional structural relationships of cellulose and its derivatives warrant the assumption that the complex (*c*) may act as a solvent of the ionised groups (*a*) and (*b*). In all reactions of cellulose, *as cellulose*, the aggregate is maintained, and with it the associated colloidal character, which also implies structural integrity in the sense in which this has been defined above. Reactions which break down the aggregate are attended by the formation of end-products of decomposition of molecular character and dimensions; but these represent a new equilibrium, and are not to be regarded as preformed in the cellulose aggregate. The cellulose aggregate is modified by the conditions under which it reacts; just as every colloidal salt in solution would be affected by every change determined in the solution, such as of temperature, dilution or concentration, the addition of 'neutral' compounds, and, of course, more profoundly, by active reagents combining specifically with its constituent groups or ions.

CHAPTER II

CELLULOSE AS A CHEMICAL INDIVIDUAL

THE discussion of the previous chapter will have suggested that our subject involves much that is undetermined if not vague or nebulous. It will be the purpose of subsequent chapters to deal with recent investigations as contributing to the elucidation of those problematical issues involved in general questions of constitution, and the actual state of matter composing the cellulose complex. They may not have been undertaken with this object immediately in view; in fact the authors' purpose is, in many cases, rather to reduce some particular phenomenon to the basis of exact quantitative expression, leaving out of consideration the issues which are vague and undetermined. But, with this empirical aim, there is a factor at work leading the authors to explore simultaneously, and with more or less set purpose, the region of theory. Now it will be generally recognised that the chemistry of cellulose and its derivatives presents a large accumulation of experimental matter, of which the quantitative relations are as exact and well grounded as those of any other section of the science; notwithstanding the fact that we are dealing with essentially uncrystallisable complexes, colloidal aggregates, in fact, of which therefore we have not the associated criteria of 'purity,' and constitutional relationships, belonging to bodies which can be examined in the 'molecular' state.

It will facilitate the object we have in view to separate such empirical data as can be briefly set out from those

which involve the undetermined elements of our subject, and which require discussion from the point of view of alternative hypotheses.

We shall therefore in this chapter give a statement of the chemical characteristics of cellulose, which may be taken as a condensed summary of the experimental facts, such as might be included in a systematic text-book of the science :

Cellulose.—Generally the non-nitrogenous skeleton of vegetable tissues. Type : the fibre-substance of cotton, purified from associated 'impurities' by processes of (1) alkaline hydrolysis and oxidation (bleaching); (2) of digestion with hydrofluoric acid, &c., to remove mineral impurity.

Composition.—Elementary $\begin{Bmatrix} C & 44{\cdot}4 \\ H & 6{\cdot}2 \\ O & 49{\cdot}4 \end{Bmatrix}$, whence the empirical formula $C_6H_{10}O_5$.

Constitution undetermined.—Is variously regarded as :

(1) Polyhexose (anhydride) $<$ Aldose. / Ketose.

(2) Polycyclohexane derivative.

(3) An aggregate of groups of variable and undetermined dimensions, of which only the ultimate terms are known, viz. CH_2OH, CHOH, CO ; but the anhydride forms of the alcoholic OH groups, and the position or positions of the CO groups, remain undetermined.

Constitutional moisture.—Is retained by the cellulose in its air-dry state, varying between 6 and 8 p.ct. according to temperature and saturation of surrounding air.

Solvents.—Cellulose is insoluble in all neutral solvent liquids. Is dissolved by :

(1) Concentrated solutions of zinc chloride, on heating at 80° to 100°.

(2) Solution of zinc chloride (1 part) in concentrated hydrochloric acid (2 parts) in the cold.

(3) Solution of cupric oxide (hydrate) in aqueous ammonia, in the cold. The cellulose may be recovered quantitatively from these solutions, though constitutionally changed.

Reactions.—The above reactions resulting in solution of the cellulose are characteristic; otherwise it is exceptionally non-reactive. By dilute solutions of iodine, in presence of certain dehydrating agents, it is coloured blue.

A. **Cellulose Compounds, i.e. Synthetical Derivatives.—Esters.** (*a*) NITRATES.—By direct reaction with nitric acid, usually in presence of sulphuric acid, in which case unstable mixed esters are formed as a stage in the reaction, the NO_3 displacing the SO_4H residues. The esters are formed without sensible structural modification. They are purified from residual SO_4H by prolonged boiling with water, and are then 'stable.' A series of these esters are known, the highest approximating to the trinitrate (C_6) (gun-cotton) the intermediate terms—dinitrate—being soluble in ether-alcohol (collodion cotton), the lowest having physical properties but little different from the original cellulose.

These esters are variously formulated as nitrates of a reactive unit of C_6—C_{12}—C_{24} dimensions.

Solvents.—The special solvents of these esters are acetone, ether-alcohol, nitrobenzene.

Saponification.—By certain alkaline and reducing agents (alkaline sulphydrates) the nitric groups are eliminated and cellulose regenerated.

(*b*) ACETATES.—By reaction with acetic anhydride under various conditions: (1) At 110°; direct formation of monoacetate (C_6) insoluble in all neutral solvents and in the solvents of cellulose. (2) At 140° to 160°; formation of higher

acetates, attended by solution in the reaction mixture. (3) In presence of catalytic agents ($ZnCl_2$—H_2SO_4—H_3PO_4) at intermediate temperatures; H_2SO_4 determines reaction at 25° to 35°. The products are usually mixtures of tri- and tetracetate. (4) When the reaction mixtures are diluted with hydrocarbon the fibrous cellulose may be acetylated without solution or sensible structural change.

Solvents of the higher acetates, chloroform, acetone, phenol.

Saponification.—The acetyl groups may be removed by boiling with alkaline solutions, the cellulose being regenerated. In quantitative determinations the saponification may be effected by boiling with normal sodium hydrate diluted with an equal volume of alcohol.

(*c*) ACID-SULPHURIC ESTERS.—By the action of sulphuric acid an extended series of esters is formed, which have been described as cellulose sulphuric acids. But they are certainly derivatives of products of resolution. The first stage results in the formation of a disulphuric ester $C_6H_8O_3(SO_4H)_2$, but its relationship to the parent complex is doubtful. The ester is soluble in water; the Ca, Ba, and Pb salts are insoluble in alcohol. By progressive hydrolysis the cellulose is ultimately resolved to dextrose.

(*d*) ACETO-SULPHATES AND MIXED ESTERS, containing the SO_4H residues associated with acetyl and other negative groups in combination, are obtained when sulphuric acid is allowed to act under regulated conditions simultaneously with other esterifying agents. Thus a mixture of acetic anhydride (50 parts), glacial acetic acid (50 parts), and sulphuric acid (4 to 6 parts), acts rapidly at 30° to 40°. The first product appears to be a neutral body of the empirical formula,

$$[4.C_6H_7O]SO_4[C_2H_3O_2]_{10},$$

and under the action of water to undergo an internal hydrolysis, the SO_4 group becoming SO_4H, which forms a stable combination with bases. The Mg, Ca, Zn salts are insoluble in water, but soluble in acetone (see p. 88).

(*e*) BENZOATES result from the action of benzoyl chloride in presence of alkaline hydrates. A monobenzoate (C_6) is obtained by treating cellulose with a solution of sodium hydrate of 10 p.ct. (NaOH) strength, and shaking with benzoyl chloride. This benzoate is formed with only slight structural change. The dibenzoate (C_6) is obtained by the interaction of benzoyl chloride and alkali-cellulose (mercerised cotton) in presence of sodium hydrate solution (15 p.ct. NaOH). Its formation is attended by structural change: the fibrous cellulose is disintegrated, the dibenzoate being an amorphous substance. The dibenzoate is soluble in acetic acid, chloroform.

MIXED ESTERS, containing the benzoyl and nitric residues, result from the action of nitric acid upon the benzoates. Simultaneously a nitro-group enters the benzoyl residue.

ALKALI CELLULOSE.—The fibrous cellulose undergoes considerable structural modification under the action of solutions of sodium hydrate of 12 to 25 p.ct. NaOH. There is a definite synthetical reaction in the ratio $C_6H_{10}O_5 : 2NaOH$, which is a stage in the formation of the dibenzoate (*supra*).

The compound is completely dissociated by water; by treatment with acohol an equilibrium is reached when the reagents are associated in the ratio $C_{12}H_{20}O_{10}NaOH$

The alkali-cellulose hydrate, of composition

Cellulose . .	30	Cellulose : Sodium hydrate,
Sodium hydrate .	15	$C_6H_{10}O_5$ $2NaOH$
Water . . .	55	

is the first stage in the synthesis of *cellulose xanthogenic* acid,

which results from the interaction of the alkali cellulose and carbon disulphide at ordinary temperatures. The sodium salt is soluble in water. It is an unstable compound, the solution undergoing spontaneous progressive change. The solution, which is highly colloidal, finally solidifies. By reason of the characteristic reaction of the xanthates with iodine,

$$CS\begin{matrix}OX\\SNa\end{matrix}\ \begin{matrix}XO\\NaS\end{matrix}CS + I_2 = 2NaI + CS\left\langle\begin{matrix}OX-XO\\S - S\end{matrix}\right\rangle CS,$$

the progress of the change may be followed, the essential feature being the elimination of the CS_2 residues with re-aggregation of the cellulose units. Well-marked stages in the series occur at the points denoted by the empirical formulæ $C_{12}H_{19}O_9CSSNa$, $C_{24}H_{39}O_{19}CSSNa$. The former represents an equilibrium attained after the solution has remained for some hours at the ordinary temperature; the latter is reached in from three to four days. The cellulose under the reaction acquires a more acid character, an additional OH group combining with alkali. The lower terms of the series, though insoluble in water or dilute saline solutions, are dissolved by the addition of sodium hydrate. The sodium atom in combination with the CSS residue is not attacked by weak acids, such as acetic acid. By double decomposition with soluble salts of Cn, Zn, &c., the corresponding xanthates are produced as insoluble colloidal precipitates.

In the above reactions the cellulose aggregate is maintained; the solutions of the derivatives are viscous and colloidal; but in the following

B. **Reactions of decomposition,** which are determined by hydrolytic and oxidising agents, the directions of resolution are extremely various and the relationships of the products to the original aggregate are undetermined.

(*a*) Sulphuric Acid, sp.gr. 1·55–1·65, dissolves the cellulose as a disulphuric ester; but decomposition attends the reaction, and on diluting and boiling the hydrolysis is carried to the extreme molecular limit, the final product being dextrose.

(*b*) Hydrobromic Acid in ethereal solution attacks the cellulose profoundly with production of brom-methyl furfural. The formation of this compound indicates a previous or intermediate stage in which the products of resolution are molecular ketonic bodies of carbohydrate constitution.

(*c*) Hydrochloric Acid in presence of water, dilute sulphuric acid, and acids generally, attacks the cellulose aggregate with production of a variety of derivatives. (1) *Insoluble*: These are generally termed hydrocelluloses. They are disintegrated residues of the original fibres; they differ chemically from the parent aggregate in the presence of free aldehydic groups, and in readily yielding to the action of alkalis. (2) *Soluble* molecular products, chiefly dextrins and dextrose.

(*d*) Alkaline Hydrates and Alkalis generally have little action on cellulose in the form of dilute solutions—even when treated at elevated temperatures. Sodium hydrate in solution of concentrations of 12 p.ct. NaOH and upwards, combines with the cellulose, producing profound structural modifications (mercerisation), but without resolving the aggregate.

At higher concentration and temperature the cellulose is partially dissolved; but even under the conditions of a 'fusion' at 180° the resolution is limited to the conversion into alkali soluble modifications, which are precipitated in the colloidal form on diluting and acidifying. At higher temperatures (250°) and with larger proportions of the alkaline hydrates, the cellulose is resolved into acid products of low molecular weight, chiefly acetic acid and oxalic acid.

OXIDANTS.—The directions of oxidation of cellulose are likewise extremely diversified. The aggregate manifests considerable resistance to alkaline oxidants in dilute form, e.g. solutions of the *hypochlorites*, *permanganates*; but when the limit is passed the oxidations which result are drastic in the sense that the soluble products are of low molecular weight, chiefly carbonic and oxalic acids. The insoluble fibrous residues, more or less disintegrated, are known as oxycelluloses. They contain free aldehydic groups, are easily attacked by hydrolysing agents, and on boiling with hydrochloric acid (1·06 sp.gr.) are decomposed with production of some furfural.

Resolved by the action of *concentrated* solutions of the *hypochlorites*, cellulose yields chloroform and carbon-tetrachloride. The hypobromites give the corresponding bromine derivatives. Nitric acid (1·25 sp.gr.) at 180° converts cellulose into a series of 'oxycelluloses,' which are resolved on boiling with calcium hydrate into acid products, among which isosaccharinic and dioxybutyric acids have been identified. In the original oxidation small quantities of the higher dibasic acids—saccharic and tartaric acids—are produced, but the main products are oxalic and carbonic acids.

With *chromic acid* an endless series of oxidations may be effected, the degree of action depending upon the proportion of the active oxidant and the associated hydrolytic action of mineral acids. The oxycelluloses produced are distinguished by relatively large yield of furfural when decomposed by boiling HCl.Aq (1·06 sp.gr.). In presence of sulphuric acid there ensues complete combustion, and the reaction is the basis of quantitative analytical methods.

RESOLUTION BY FERMENT ACTIONS.—Under the actions of specific organisms the cellulose complex is totally resolved, the main products being methane, hydrogen, and carbonic and fatty acids. The decomposition may be associated with the

action of an enzyme; but a remarkable feature of the process is the absence of intermediate products, at least in the cases hitherto investigated. In the digestive tract of the herbivora cellulose is resolved, and from the investigation of the process, necessarily by indirect observations, it appears that, in addition to a destructive resolution to ultimate gaseous products, there occurs a resolution to proximate groups of high nutritive value, which are assimilated by the animal organism.

RESOLUTION BY HEAT; DESTRUCTIVE DISTILLATION.—The decompositions of cellulose at temperatures exceeding 250° are necessarily extremely complex.

The groups of products show an average proportion:

Solid 30 p.ct.	Liquid 50 p.ct.	Gaseous 20 p.ct.
Charcoal or pseudo-carbon	Containing Acetic acid (2 p.ct.) Methyl spirit (7 p.ct.) Acetone, furfural tar (12 p.ct.)	Chiefly CO and CO_2

the actual proportions and composition of these mixtures varying with the temperature and duration of the heating.

GENERAL VIEW OF THE DECOMPOSITIONS OF CELLULOSE.—It is clear that the cellulose complex breaks down under destructive influences, in directions depending upon the nature of the attacking agent, its concentration, and all the surrounding physical conditions. The study of these decompositions has thrown but little light on the actual nature and constitution of the cellulose aggregate: for the reason, perhaps, that we have endeavoured to maintain a basis of interpretation such as is applicable to ordinary molecular compounds or complexes. If we regard cellulose as the analogue of a complex salt in presence of water, and endeavour

to follow the reactions of decomposition as we should the changing equilibrium of a *colloidal salt solution* under the action of reagents, we have a basis of working hypotheses which will be found to stand the general test of credibility—that is, they tend to progress in investigation. We make this observation in reference to the matter which we have just endeavoured to reduce to short, systematic expression, but which obviously cannot effectually be so treated because it involves the entire theoretical basis of our subject, that is, the actual state of matter and the distribution of the reactive unit-groups in the cellulose complex; and this basis is, as yet, entirely undetermined.

The Cellulose Group.—From the typical cellulose we pass to the diversified *group of celluloses.* Their general characteristics are those of the prototype; the variations they present are especially such as involve the undetermined factors of constitution. With these there are certain correlative variations which afford an empirical basis of classification. These are (*a*) the degree of resistance to hydrolytic and to oxidising agents, (*b*) the percentage yield of furfural when decomposed by boiling HCl.Aq, (*c*) elementary composition, in respect of the ratio C : O.

The fibrous celluloses are grouped as follows:

Type	Cotton sub-group. A. Bleached cotton	Wood cellulose sub-group. B. Jute cellulose	Cereal cellulose sub-group. C. Straw cellulose
Elementary composition C.	44·0–44·4	43·0–43·5	41·5–42·5
Elementary composition O	50·0	51·0	53·0
Furfural	0·1–0·4	3·0–6·0	12·0–15·0
Other characteristics	No active CO groups	Some free CO groups	Considerable reactivity of CO groups

Of these groups the following points may be noted:

A. Comprises, in addition to cotton, other industrially important celluloses, e.g. flax, hemp, and rhea. They occur in the plant-world in association with compounds easily removed by the action of alkalis. They pass through the cycle of reactions involved in their solution as xanthate, without hydrolysis to soluble derivatives.

B. These celluloses are obtained as products of decomposition of a compound cellulose. They may be regarded as partially hydrated or hydrolysed. They are more readily attacked by hydrolysing agents and, in the xanthate reactions, are partially resolved to alkali-soluble derivatives.

C. These celluloses are in most cases a complex of structural elements, and not homogeneous chemically. They are still less resistant than the preceding group, and more especially the furfural-yielding components which are selectively attacked under certain conditions.

The cellulose groups, as above, pass by imperceptible gradations into a heterogenous class of natural products which, while possessing some of the characteristics of the celluloses proper, are so readily resolved by hydrolytic treatment that they must represent a very different constitutional type or types. To this group of complex carbohydrates the class-name **hemicellulose** has been assigned. They are structurally different from the fibrous celluloses, occurring mostly in the cellular form (parenchyma, &c.). They differ in physiological function and in being readily resolved by hydrolysis into the crystalline monoses.

CHAPTER III

CELLULOSE AND STRUCTURAL FORMS—DIMENSIONS

THE celluloses are produced in definite structural forms; and since questions of form and dimensions therefore continually confront the student, we present in this chapter some of their more important aspects, with conclusions as to their immediate bearings upon the investigations of the near future.

We may, as a preface, set out the dimensions of the more important celluloses, considered as ultimate fibres:

—		Length of fibre	Diameter
Fine textiles	Cotton . .	20–40 mm.	—
	Flax . . .	25–30 ,,	0·015–0·037
	Rhea . . .	60–200 ,,	0·030–0·070
	Hemp . .	15–25 ,,	0·016–0·050
Coarse textiles and rope-making	Jute . . .	1·5–4·0 ,,	0·020–0·025
	Sisal . . .	1·5–6·0 ,,	0·015–0·026
	Phormium . .	5·0–15·0 ,,	0·010–0·020
	Pinewood . (Tracheids)	1·0–2·0 ,,	0·015–0·020
Paper-making	Esparto .	0·5–3·0 ,,	0·010–0·018

Only in the exceptional case of cotton is the 'ultimate fibre' the naturally occurring form of the fibre substance. The general case is that of a fibre bundle, simple in the case of flax, hemp; more complex in the case of jute and the fibro-vascular bundles of monocotyledons; and a heterogeneous aggregate in the case of esparto and many of the woods. With the more complex structure the celluloses are associated with various chemical groups (compound cellu-

loses), which are attacked and removed by the various treatments of hydrolysis and oxidation by which the celluloses are isolated. For our present purpose we are concerned only with the celluloses in the form of ultimate fibres. These are the unit elements of structure of the yarns and threads which are the basis of textile fabrics; and the mechanical properties of these, as well as the processes by which they are mechanically prepared and ultimately spun, are obviously determined by their simpler elements of form—that is, their dimensions. The mechanical principles involved in the production of fine textile yarns from these discontinuous units are, first, the reduction of these to a continuous untwisted sliver, in which they are parallelised; secondly, the drawing and twisting of the fibres composing the sliver in continuous length. The tensile properties of the resulting yarn depend mainly upon the twist, partly upon the adhesion of the more or less closely spun fibres. There are numerous variations of the process, such as the wet spinning applied to the bast fibres and notably flax, the passage of the sliver through a bath of warm water facilitating the ultimate sub-division of the bundles of fibres. In the coarser textiles, such as jute, it is evident that the spinning unit is an aggregate or bundle of the ultimate fibres, which are too short (2 to 3 mm.) to admit of manipulation.

We are only concerned with this general and superficial view of spinning processes in passing to the main subject of this chapter, which is the tensile characteristics of the 'artificial silks' or lustracelluloses. In these we have the common feature of a solution of cellulose, i.e. of a cellulose compound, drawn at uniform speed through a fine orifice and solidified in continuous length. The resulting thread may be regarded as structureless and of more or less regular dimensions. The mechanical properties of such a thread—resistance to strain, elasticity, and extensibility—are therefore properties of the

cellulose substance independently of grosser structural details such as characterise the 'natural' cellulose fibres. Moreover, the regularity of form gives a particular precision to the measurements of tensile properties. We are thus able to formulate a normal basis of investigation from which the whole of the physical properties of the celluloses may be inquired into with some prospect of revealing the relationships of external or visible form to the invisible units or aggregates of which the fibre substance is made up.

A few illustrations will indicate the directions of inquiry. The 'artifical silks' are classified for relative fineness on the basis of the metrical weight-length units which are used in the silk industry. The 'denier' (metrical) represents the weight in milligrammes of the unit length, viz. 10 metres. It applies equally to the single filament (brin) or to the assemblage of these—usually from 10 to 20, which make up the weaving unit. In speaking therefore of a yarn of 80 deniers having a 'tenacity' of 96 grms. and an 'elasticity' of 12, we are shortly expressing the ultimate facts as follows:

The yarn weighs 0·080 grm. per 10-metre length, and breaks when stretched with a weight of 96 grms., having undergone an elongation of 12 p.ct. in length. Assuming 16 unit filaments in the yarn, each is of 5 deniers and would bear $\frac{1}{16}$ of the stretching weight. Taking an average diameter of the unit at 0·03 mm., this implies a sectional area of 0·000707 mm.□; and the tenacity may therefore be expressed as being equal to

$$\frac{6}{0\cdot000707} = 8{,}486 \text{ grms. per mm.}\square,$$

which at once conveys the relationship of cellulose to other structural materials which are capable of being produced as a regular solid in continuous length, e.g. the metals.

Another form of expression which has advantages in comparing structural quality is the *breaking length*—that is, the

length of the material which, supposed extended in space, will determine fracture ; in the above case

$$\frac{96{,}000 \times 10}{80} = 12{,}000 \text{ metres.}$$

We may compare this figure with the average numbers for the standard cellulose textile yarns taken from a recent work by a leading authority, 'Papierstoffgarne,' Prof. E. Pfuhl, Riga, 1904.

—		Breaking length	Extensibility
		km.	p.ct.
Cotton yarns		13–14	3·97
Ramie		11–12	0·79–1·95
Flax ('line') (wet spun)		12·4–19·5	1·1–1·78
Flax yarns (dry spun)		11·8–12·4	2·5–3·67
Jute yarns		9·76	2·0
Lustracellulose	Average	12	10
	Extremes	8·0–14·0	7–18

Apart from the practical significance of these comparisons, they supply the basis for an analytical estimate of the various factors which contribute to structural quality. In the case of the natural fibres these additional factors are the twist of the yarn and the apposition of the surfaces of the component fibres, which, again, will be affected by their minute structure.

These questions graduate, in another direction, into the problem of the actual structure of papers and the fibre agglomerates produced by the paper-making process. A paper is a continuous web composed of discontinuous fibres, which require to be milled or brought by mechanical treatment within a certain somewhat narrow range of lengths, viz. 1 to 3 mm. The strength of the dried web or agglomerate depends upon the interlacing of the fibrous units, and the adhesion of their surfaces, which latter factor is largely influenced by the colloidal properties of the fibre substance, as well as by the co-operative action of structureless hydrated colloids, either derived from

the fibre substance or added in the form of sizing agents. The mechanical properties of papers are expressed in the same terms as those of the textile yarns, and it is interesting to compare the range of numbers for the highest classes of papers:

—	Breaking length	Elongation
	metres	p.ct.
Rag papers, manila papers, and wood-pulp papers (air dry)	4,000–8,000	3–8

It is evident from these numbers that the aggregation of shorter units by the paper-making process produces a texture approximating in mechanical properties to the lower grades of spun yarns. It is only necessary to change the form or dimensions of the aggregate from the plane to the cylindrical to produce a yarn available for weaving. An industry based upon these principles is being actively developed, a full account of which will be found in the recent work of Professor E. Pfuhl, 'Papierstoffgarne,' which we have previously cited.

In addition to the conversion by a rolling process of the flat strips into the cylindrical form, these are subjected to a twisting process while still in a moist condition, with the effect of increasing the solidity and resistance of the agglomerate This is illustrated by the following comparative numbers:

—	Breaking length	Elongation
	km.	p.ct.
Plane strips—dried	4·17	2·84
Rolled into cylindrical form . .	5·18	2·71
Rolled and twisted	6·41	3·06

It is perhaps scarcely necessary to state that yarns of this class show a very large reduction in tenacity when wetted with water, and their range of application is proportionately limited. The same want of resistance, though to a less extent, also

limits the usefulness of the lustracelluloses. We are, however, not concerned at the moment with industrial questions, but with ultimate structural phenomena. The action of water in the two cases, though similar in effect, is obviously referable to different proximate causes. The action on the fibre-aggregate is to break up the adhesion of the fibre surfaces by the penetration or imbibition of the liquid; but the cellulose of the 'artificial silks' is affected by actual combination with water or hydration, which may be regarded as an incipient solution. Of the ultimate phenomena which are concerned we can only, at present, form vague and conjectural pictures. But the subject will not remain in this condition of indefiniteness, for the special properties of the lustracelluloses, and generally of the artificial structureless forms of cellulose, supply a new basis for the accumulation of exact measurements. This is especially the case in regard to the entire range of hydration phenomena, in which the incipient stages are connoted by the expression 'hygroscopic moisture,' or the corresponding French term 'humidité'—that is, the property of taking up from the atmosphere and retaining a proportion of water.

The proportion of water which the celluloses retain in the air-dry condition is not only a 'constitutional' fact, but an important factor of their mechanical properties.

Some observers, who have investigated these phenomena from a more special point of view, have arrived at different conclusions; and we shall have occasion to note (see p. 71) more particularly the researches of Orme Masson 'On the Wetting of Cotton by Water and by Water Vapour' (Proc. R.S. 1904, p. 230). From a close study of the associated thermal effects Masson concludes 'that the heat produced by the absorption is of about the same magnitude as the heat of liquefaction of the same quantity of water'; and, after discussing the

bearings of this central fact, 'the view that the water becomes chemically combined to form definite hydrates of cellulose may be quickly dismissed, as there are no facts to support it.'

We shall deal subsequently (p. 81) with the evidence which Masson regards as non-existent; but at the moment we are concerned with an incidental discussion which follows the above statement. The author has to deal with the supposition that the moisture is deposited and held as a surface-film. He arrives at an approximate estimate of the actual surface of a given mass of cotton 'on the assumption that the fibres are uniform cylinders of such length that the ends are negligible,' in which case the surface or area is $4w / 1{\cdot}525 \times 188 \times 10^{-5}$, in which expression w is the weight, 1·525 the sp.gr. of the cotton substance, and 188×10^{-5} c.m. the average diameter of the fibre.

To those who are familiar with the minute structure of the cotton fibre—its large and irregular variation from the cylindrical form, and the complicated details of its imbricated interior texture—it is evident that the assumption is subject to errors so large as to invalidate any calculation of volume or surface. It is true that the author only employs it in disposing of an incidental point, and is evidently aware of its uncertainty. But we may, without these elements of uncertainty, apply the calculation to the artificial cellulose tissues, more particularly to the lustracellulose obtained from aqueous solutions of cellulose, since these are of approximately regular form. Thus, taking 1·500 as the sp.gr. of the air-dry product, D the diameter of the unit thread, w the weight of a given mass:

The surfaces of a given length, L, is π D L and the weight

$$w = \frac{\pi D^2}{4} L \times 1{\cdot}5$$

so that the surface s, of a given weight w, is $w \dfrac{4}{D \times 1{\cdot}5}$.

From these elementary facts and relations an extensive range of investigation is opened out.

In the first place, the two obvious factors of the combination of the celluloses with atmospheric moisture can be separately varied. The water must be taken up at the limiting surface, and the rate of combination must vary in proportion to surface. But the total complement of 'moisture' represents a property of the *fibre-substance*; the substance is penetrated by the water molecules, and presumably by osmotic diffusion. This is fully recognised by Masson (p. 252, *loc. cit.*) and the combination, he says, 'may be regarded as a solid solution of cellulose and water.' With an irregular solid such as cotton, and no measurement of surface of which the errors can be even approximately quantified, the investigation of the simplest of such phenomena is rendered much more difficult. The methods and results described in this interesting paper must therefore be complemented by observations upon the regular forms of the 'artificial cellulose'—fibres, films, and larger masses—and the results must certainly tend to a closer knowledge of the mechanism of the reactions.

But we are not limited to observations upon cellulose; we may extend them to the compounds of cellulose such as can be brought into homogeneous solution; notably to the nitrates and acetates. Reverting for a moment to the discussion of the earlier part of this chapter, we pointed out that the more purely mechanical properties are reducible to very exact expression in the case of homogeneous structureless solids producible in regular form, and of dimensions varied at will. It is evident that a study of derivatives which can further be varied at will, over a wide range of compound forms, must contribute to a knowledge of the, as yet, obscure conditions of the solid state. It might be supposed that chemical con-

stitution is not causally related to structural properties; and a superficial view of these forms of cellulose and derivatives of the closest external resemblance and of similar structural properties, would appear to confirm the impression. But, as chemists, we cannot limit our views to the proximate and visible forms of matter. We can only think in terms of ultimate constituent groups; and we must put the question whether these are possibly related to the visible forms of the apparently homogeneous matter? In the case of the cellulose group we are certainly able to affirm that stuctural modifications accompany definite chemical changes in the cellulose complex; and such modifications persist in the derivative compounds obtained from such modified celluloses. Admitting that these experimental facts introduce structural relationships, we must pass to the *à priori* generalisation, upon which basis we are confronted by the following problems: (1) Are the structural properties of the celluloses definitely related to their ultimate configuration, in the chemical sense? (2) If so, is the relationship dominated by the arrangement of the carbon atoms, or are the hydroxyl groups more particularly involved? or (3) Is the causal connection to be found in the superior grades of aggregation or proximate constituent complexes of unascertained dimensions?

The evidence at present available points to the latter conclusion, but also indicates that the hydroxyl groups are not essentially involved, since the esters have generally the same colloidal and structural properties as the parent celluloses. Lastly, we find that with the colloidal properties of cellulose, while there is much in common with the colloids generally, there are specific characteristics which may be assumed to be correlated with the grouping of the carbon atoms.

We shall deal with the evidence which has so far accumulated, in later sections. The purpose of this chapter is limited

to the broad statement of a case for the pursuit of problems of structure, from the grosser limits, through the range of minuter dimensions requiring microscopic measurements, to the ultimate details of the invisible structural units. We have no wish to anticipate the results of investigations, nor even to forecast in definite terms the lines of work which, in our opinion, are best calculated to contribute to the evolution of the subject.

SECTION II

We proceed to the contributions of experimental matter, of which we shall give an account in the form of abstracts, retaining the several authors' particular views in detailing the substance of their communications, following with a critical discussion of their results from the standpoint of the views which we have set out in the earlier chapters.

A. Synthetical Derivatives—Hydroxyl Reactions: Esters.

Of the esters of cellulose the most important are the nitrates; and the following are the more important contributions to the fundamental chemistry of these derivatives:

1.

RESEARCHES ON NITROCELLULOSE.

G. Lunge (J. Amer. Chem. Soc. 1901, 23, 527).

This paper embodies the results of extensive investigations during the period 1897–1900, in which the author has had the co-operation of Weintraub and Bebie (Ztsch. angew. Chem. 1899, 441–467 *et seq.*).

The object of the investigations 'was to study the conditions under which nitrocelluloses of various compositions and various properties can be regularly and with certainty

prepared, and to establish both the composition and the properties of the products obtained under varying circumstances with greater accuracy than has been done up to this time, as witnessed by the considerable discrepancies among the statements of different authorities.'

The form of cellulose nitrated was the so-called 'chemically pure surgical cotton-wool,' further purified by boiling with a weak solution of sodium carbonate and, after thorough washing, extracting with alcohol and ether. The preparation was found to retain 0·06 p.ct. of ash constituents.

The details of control of the original reaction, of purification of the products, and of the analytical methods employed are fully described in the two first sections of the paper. These are for the most part based upon the standard methods, with such variations and refinements as were necessary to ensure the highest degree of uniformity and accuracy.

The author's method for the 'estimation of unchanged cellulose in nitrocelluloses' may be mentioned at greater length. It is based on the observation that sodium ethylate, which has no effect upon cellulose, 'decomposes the nitrocelluloses almost instantaneously, forming a reddish-brown substance soluble in water.' The reagent is prepared by dissolving 2 to 3 grms. of sodium in 100 c.c. ethyl alcohol (95 p.ct.), and diluting with 100 c.c. acetone. Five grms. of the nitrocellulose are digested with the reagent at the ordinary temperature for some hours, or heated at 40° to 50° for 20 to 30 minutes. The residue is washed with alcohol and then with water, and finally dried and weighed. It is noted that the method is not applicable to nitrates of lower nitrogen percentage, owing to variations in the results, amounting to 5 or even 10 p.ct.

The section reviewing the history of the 'methods for obtaining the various nitrocelluloses' deals with the funda-

mental question of the actual reacting unit of cellulose, in the following terms :

'The first chemists who worked on nitrocelluloses adopted for cellulose the formula $C_6H_{10}O_5$, and consequently spoke of "trinitrocellulose," $C_6H_7(NO_2)_3O_5$, as the highest obtainable term, while "dinitrocellulose," $C_5H_3(NO_2)_2O_5$, was supposed to represent the composition of "soluble" nitrocellulose. The former expression is still sometimes used to denote gun-cotton (pyroxylin), the latter for denoting collodion cotton.

'Of course it has been known for a long time past that the molecule of cellulose must be a multiple of $C_6H_{10}O_5$, but its real magnitude is not known and is not of much importance in this connection. All we need is to fix the lowest figure by which we can represent the various products obtainable by introducing NO_2 groups (nitric acid radicals) into the molecule of cellulose.

'Eder[1] obtained four degrees of nitration from the highest downwards, and consequently doubled the ancient formula, as he required the molecule $C_{12}H_{20}O_{10}$ to represent all his products. Vieille,[2] however, obtained within the same limits a greater number of distinct products, and found himself compelled to use the molecular formula $C_{24}H_{40}O_{20}$ for cellulose. This would cause the highest degree of nitration to be called "dodecanitrocellulose," in lieu of the old term "trinitrocellulose" or Eder's "hexanitrocellulose," but Vieille could not obtain this highest term at all and declared "endecanitrocellulose," $C_{24}H_{29}(NO_2)_{11}O_{20}$, to be the highest product of nitration obtainable. The table which follows gives the formulæ and nitrogen percentages of the various stages of nitration denoted according to the C_{24} . . . molecule, which we adopt throughout this paper as being sufficient for representing our present stage of knowledge.

[1] *Ber. d. Chem. Ges.*, 13, 169. [2] *Compt. Rend.* 95, 132.

Degrees of nitration.	Formula.	Nitrogen p.ct.	NO per 1 gram c.c.
Dodecanitrocellulose (= old trinitrocellulose)	$C_{24}H_{28}O_{20}(NO_2)_{12}$	14·16	225·53
Endecanitrocellulose	$C_{24}H_{29}O_{20}(NO_2)_{11}$	13·50	215·32
Decanitrocellulose	$C_{24}H_{30}O_{20}(NO_2)_{10}$	12·78	203·87
Enneanitrocellulose	$C_{24}H_{31}O_{20}(NO_2)_9$	11·98	191·08
Octonitrocellulose (= old dinitrocellulose)	$C_{24}H_{32}O_{20}(NO_2)_8$	11·13	177·52
Heptanitrocellulose	$C_{24}H_{33}O_{20}(NO_2)_7$	10·19	162·53
Hexanitrocellulose	$C_{24}H_{34}O_{20}(NO_2)_6$	9·17	146·26
Pentanitrocellulose	$C_{24}H_{35}O_{20}(NO_2)_5$	8·04	128·24
Tetranitrocellulose (= old mononitrocellulose)	$C_{24}H_{36}O_{20}(NO_2)_4$	6·77	108·01

'Mendelejeff[1] obtained a product containing 12·44 p.ct. nitrogen entirely soluble in ether-alcohol, whose nitrogen percentage is about midway between Vieille's deca- and ennea-nitrocellulose. Vieille had stated that deca- was insoluble, ennea- soluble, and therefore Mendelejeff considered his soluble intermediate product as a new, individual step of nitration which would compel the adoption of a formula containing C_{18}. But as we shall see later on, there exists a soluble decanitrocellulose, and there is hence no reason whatever for making the solubility of Mendelejeff's products a criterion of its nature as an individual compound; it may very well have been a mechanical mixture of the deca- and ennea-body. I do not, therefore, at present see any reason why we should write our formulas on the basis of C_{48} . . . and I shall retain the basis of C_{24} . . . by which all our results can be satisfactorily expressed. Of course, the real formula must be nC_{24} . . . , but we may neglect the unknown value of n as immaterial for our purposes.

'The lower members of the series of nitrated celluloses, up to deca-, can be obtained by means of nitric acid alone, but as even these in actual practice are always prepared by mixtures

[1] *Moniteur Scientifique*, 1897, p. 510.

of sulphuric and nitric acids, we have almost exclusively worked with such, and we shall now proceed to discuss the conditions for obtaining the various steps of nitration.'

The experimental results recorded in this communication are especially valuable for the internal evidence of accuracy, and may be accepted as establishing a number of constants of importance on the highest stage of nitration obtained from cellulose.

By the action of mixtures of the anhydrous acids the maximum stage attained was the endecanitrocellulose (N= 13·5 p.ct.) confirming Vieille (Comp. Rend. 95, 132), and Vignon (*ibid.* June 6, 1898). On the other hand the authors confirm Hoitsema's results obtained with mixtures of nitrogen pentoxide and phosphorus pentoxide, viz. the higher stages of nitration (N=13·88, 13·90) approximating to the dodecanitrocellulose (Ztsch. angew. Chem. 1898, 173).

But these higher nitrates are obtainable by varying the composition of the ordinary mixture in the direction of hydration: moreover, as direct products and without fractionation by ether-alcohol to remove lower nitrates. The following table of experimental results establishes this point:

No.	Composition of acid mixture			Nitrogen in product, p.ct.	Yield on cotton, p.ct.
	H_2SO_4	HNO_3	H_2O		
1	60·00	27·43	12·57	13·62	173
2	62·10	25·79	12·11	13·75	174
3	62·95	24·95	12·10	13·83	175
4	63·72	25·31	10·97	13·75	175
5	64·56	24·65	10·79	13·71	175
6	68·02	25·28	5·70	13·76	—
7	64·55	26·55	8·88	13·72	173
8	63·35	25·31	11·34	13·92	173

It was proved, however, that these nitrates are unstable and readily lose nitric residues until the stage of the $(NO_2)_{11}$

product is reached. The endecanitrocellulose is, in effect, the highest stable degree of nitration.

In reference to the production of this nitrate, it is important to notice that the result is not influenced by a comparatively wide range of variations of composition of the mixture $H_2SO_4 : HNO_3 : H_2O$.

Whereas in the series above recorded the ratio $H_2SO_4 : HNO_3$ has been maintained at 2·3 : 1, this is varied in the following series from 3·3 to 2 : 1, without influence on the composition of the nitrate :

No.	Composition of acid mixture			Nitrogen in nitro-cellulose, p.ct.	Yield, p.ct.
	H_2SO_4	HNO_3	H_2O		
9	75·33	22·80	1·87	13·53	176
10	74·16	22·12	3·72	13·51	175
11	72·97	21·63	5·40	13·57	—
12	69·90	20·45	9·65	13·64	177
13	68·31	20·49	11·20	13·61	176
14	67·43	19·37	13·20	13·25	172
15	67·32	32·53	0·15	13·62	176·5
16	65·41	31·34	3·25	13·57	175
17	63·75	30·80	5·45	13·63	176
18	70·68	29·31	10·01	13·68	176

It is noted that in the researches of previous investigators it has not been sufficiently recognised that there are three variables in the nitration mixture to be taken into account—the ratio $HNO_3 : H_2SO_4$, the ratio of both to water, and the presence of lower oxides of nitrogen. The neglect of one or other of these variables is an obvious defect in the investigations of Vieille and of Braby (Mém. des poudres et Salpêtres, 2, 217; 8, 111).

Maintaining the ratio $HNO_3 : H_2SO_4$ approximately constant, the effect of varying only the proportion of water

is seen in the records of the following series of determinations:

No.	Nitrogen, p.ct.	Soluble in ether-alcohol, p.ct.	Yield cotton, p.ct.	Yield * (Calc.)	Acid mixture in p.ct.		
					H_2SO_4	HNO_3	H_2O
1	13·65	1·50	177·5	178	45·31	49·07	5·62
2	13·21	5·40	176·2	175	42·61	46·01	11·38
3	12·76	22·00	—	—	41·03	44·45	14·52
4	12·58	60·00	167·0	168	40·66	43·85	15·49
5	12·31	99·14	159·0	165	40·14	43·25	16·61
6	12·05	99·84	153·0	163	39·45	42·73	17·82
7	11·59	100·02	156·5	160	38·95	42·15	18·90
8	10·93	99·82	144·2	—	38·43	41·31	20·26
9	9·76	74·22	146·0	—	37·20	40·30	22·50
10	9·31	1·15	138·9	—	36·72	39·78	23·50
11	8·40	0·61	131·2	—	35·87	38·83	25·30
12	6·50	1·73	—	—	34·41	37·17	28·42

* The numbers calculated for yields are added to the author's tables.

It may be specially noted that, as the proportion of water reaches 16 p.ct. of the mixture, there is a marked increase in its effect, and 'the group of entirely soluble (ether-alcohol) nitrocelluloses, with from 12·3 to 10·9 N p.ct., is obtained by acid mixtures ranging between 16·6 and 20·3 p.ct. water.' It is clear also that the effects attributable to small variations in the percentage of water must be taken into account in reference to the water formed in the reaction, together with the abstraction of nitric acid. It is also evident that the proportion of acid mixture to the cotton treated is an essential factor of the process.

An important practical result of the above series is that the conditions intermediate between those of Nos. 7 and 8 are those for obtaining the 'pure octonitrocellulose' with 11·13 p.ct. N entirely soluble in ether-alcohol.

'The *morphological structure* of the products is also strongly altered by an increase of water in the acid mixtures. Up to

15 p.ct. water the original structure is preserved. At 18 p.ct. water the fibres appear somewhat contracted, and the characteristic twist of the cotton fibre is lost. With more water the fibres appear to be torn open, and disaggregate into small particles, which become globular matter. This destructive action is at its maximum with 23 to 25 p.ct. water; by more dilute acids the fibrous structure is much less affected, but here also by prolonged action the fibres are split up into smaller elements.'

The *influence of temperature* is seen in the subjoined tables of results, the first relating to the production of the higher nitrates by treating cotton (2·5 grm.) with fifty times its weight of a mixture of the acids in the proportion of 1 part HNO_3 (1·52 sp.gr.) and 3 parts H_2SO_4 (1·84 sp.gr.). The temperature was progressively varied, and the effect of the time-factor was also studied:

Temperature		Nitrogen, p.ct.	Yield (Calc.)	Yield, p.ct.	Loss of cellulose, p.ct.	No.
0°	½ hour	10·71	153	152·29	trace	1
	7 hours	13·19	174	173·29	trace	2
10°	7 hours	13·37	176	175·78	—	3
15°	7 hours	13·38	176	175·61	—	4
19°	½ hour	12·72	170	166·14	—	5
	7 hours	13·39	176	175·56	—	6
40°	½ hour	13·07	173	172·32	trace	7
	7 hours	13·06	173	169·62	1·61	8
60°	½ hour	13·08	173	169·18	1·95	9
	4½ hours	13·07	173	162·05	5·67	10
80°	¼ hour	13·07	173	161·23	6·52	11
	½ hour	13·12	173	125·17	27·45	12
	3 hours	13·12	173	81·52	52·76	13

The influence of increase of temperature is seen in increased rapidity of action; at the higher temperatures the yield progressively falls, which effect does not appear to be due to a direct conversion of the cellulose into soluble products, but to a solution of nitrocellulose previously formed.

The structure of the product is also progressively modified: that obtained at 60° to 80° is a finely fibrous powder after drying.

The time-factor was more closely studied in the following series, the conditions of action being those of the preceding series, and the temperature 32°.

Time of action, minutes	Nitrogen, p.ct.
5	13·27
15	13·44
30	13·47
60	13·50
120	13·40

The observations were extended to the series of collodion cottons, using an acid mixture containing HNO_3 42·15 p.ct., H_2SO_4 38·95 p.ct., H_2O 18·90 p.ct., the results being as follows:

No.	Temperature	Time of nitration, hours	Nitrogen, p.ct.	Solubility in ether-alcohol, p.ct.	Yield, p.ct.	Calc.
14	17°	4	11·50	95·60	155·1	160
15	17°	24	11·59	99·81	156·2	160
16	40°	4	11·49	99·58	148·1	159
17	60°	1/4	11·46	99·71	146·7	159
18	60°	4	10·81	99·84	152·0	154

The influence of rise of temperature on the yield of product, and also upon its structural characteristics, are more pronounced. On the latter point the author observes 'the change of structure seems to have ulterior consequences for, as I am informed upon reliable practical authority, the collodion cotton made at such high temperatures does not yield vegetable fibre fit for spinning. Probably, simultaneously with the change of morphological structure the cellulose molecule is also changed.'

The effects of varying the proportion of sulphuric acid to nitric acid have been the subject of an extended series of

experiments, the general conclusions from which are that an optimum lies within the range $H_2SO_4 : HNO_3 = 0{\cdot}25–3{\cdot}00 : 1$. Outside this range the degree of nitration is adversely affected, with progressive and proportionate structural modifications of the fibre. When the ratio $H_2SO_4 : HNO_3$ exceeds 7 : 1 the fibres are destroyed, and on drying pass into a finely fibrous powder. The quantitative results are set forth in the subjoined tables :

TABLE I.

Nitric acid	Sulphuric acid	One-half hour		Twenty-four hours		Three days	
		Nitrogen, p.ct.	Yield, p.ct.	Nitrogen, p.ct.	Yield, p.ct.	Nitrogen, p.ct.	Yield, p.ct.
1	0	12·58	162·75	12·62	163·32	—	—
1	$\frac{1}{10}$	—	—	12·66	165·02	—	—
1	$\frac{1}{4}$	13·45	175·69	13·44	175·77	—	—
1	$\frac{1}{2}$	—	—	13·42	175·22	—	—
1	1	13·36	174·56	13·39	174·75	—	—
1	2	13·23	174·14	13·32	175·98	—	—
1	3	12·72	166·14	13·40	176·44	13·38	175·55
1	4	—	—	13·20	175·12	—	—
1	5	8·14	130·88 (25·44 unchanged cellulose)	13·10	166·60	—	—

TABLE II.

Nitric acid	Sulphuric acid	Three days			Eight days			Fifteen days		
		Nitrogen, p.ct.	Yield, p.ct.	Unchanged cellulose, p.ct.	Nitrogen, p.ct.	Yield, p.ct.	Unchanged cellulose, p.ct.	Nitrogen, p.ct.	Yield, p.ct.	Unchanged cellulose, p.ct.
1	6	12·63	162·40	0·85	—	—	—	12·74	169·80	none
1	7	10·86	151·60	10·46	—	—	—	—	—	—
								Thirty days.		
1	8	—	—	—	10·88	144·62	10·7	11·70	152·0	4·48
1	9	77·4	120·11	much	—	—	—	—	—	—
1	10	—	—	—	5·43	65·0	41·12	—	—	—

TABLE III. (COLLODION NITRATES).

No.	Nitrating mixture				Product				Proportion of HNO_3 in acids to 1 cellulose
	Parts H_2SO_4 to 1 part HNO_3	H_2SO_4 p.ct.	HNO_3 p.ct.	H_2O p.ct.	Nitrogen, p.ct.	Solubility in ether-alcohol, p.ct.	Yield, p.ct.	Yield (Calc.)	
1	3	62·18	21·91	15·91	13·21	3·20	174	174	30
2	3	61·53	20·02	18·45	12·42	98·70	160	167	30
3	3	60·30	19·71	19·99	11·72	99·28	157	160	30
4	3	58·88	19·60	21·52	10·96	99·50	148	—	30
5	3	59·77	20·94	19·29	11·74	99·98	159	—	12
6	3	58·34	20·62	21·04	10·90	99·20	149	—	12
7	3·8	63·84	16·96	19·20	12·08	—	163	—	30
8	3·8	62·52	16·46	21·02	11·23	—	153	—	30
9	3·8	63·84	16·96	19·20	11·76	—	156	—	12
10	3·8	62·52	16·46	21·02	10·99	—	151	—	12
11	5	67·60	13·66	18·74	12·43	—	167	167	30
12	5	66·37	13·04	20·59	11·66	—	148	160	30
13	5	64·85	14·90	20·25	10·53	—	140	112	8
14	5	64·11	13·62	22·27	9·35	—	—	—	8

The latter affords an interesting comparison with a preceding series, also directed to the production of collodion cottons, in which the proportion $H_2SO_4 : HNO_3$ was maintained at approximately 1 : 1. The duration of the nitration was 24 hours, at the ordinary temperature. Experiments on the influence of this factor showed that at 35° exactly the same results were attainable in 2 hours. It is to be specially noted that the influence of water is the same, in proportionate effect, as in the case of the mixtures of H_2SO_4 and HNO_3 at 1 : 1.

A general account is then given of a series of nitrations in which the starting-point was HNO_3 of 1·4 sp.gr. The action of this acid is thus described: 'It causes a partial nitration, but about 63 p.ct. of the cellulose remained unchanged, no oxycellulose being formed here. The product as a whole contained 1·49 p.ct. nitrogen, and the nitrated

product alone by calculation 4·00 p.ct., which corresponds to dinitrocellulose (C_{24}). As this product has never been obtained elsewhere, many attempts were made to isolate it by the action of solvents, or to prepare it otherwise in a purer state, but in vain. By addition of 5 p.ct. H_2SO_4 some oxycellulose was formed. The product contained about 58 p.ct. unchanged cellulose and 2·15 p.ct. nitrogen; trinitrocellulose (C_{24}) would contain 5·36 p.ct. nitrogen. Here as well it was not found possible to isolate the products as a chemical individual.'

In the following series the conditions were reached in which no unchanged cellulose remained in the products. The H_2SO_4 was varied, the proportion of HNO_3 and H_2O being maintained constant at 25 and 24 parts respectively to 1 part cellulose:

No.	Acid mixture			Product		Yield, p.ct.
	H_2SO_4 p.ct.	HNO_3 p.ct.	H_2O p.ct.	Nitrogen, p.ct.	Solubility, p.ct.	
15	41·86	35·82	22·32	9·27	14·22	134
16	38·47	40·19	21·34	10·32	92·30	142
17	40·83	38·72	20·45	10·76	98·24	151
18	42·92	37·40	19·68	11·02	98·90	153
19	48·03	34·18	17·79	12·23	99·58	155
20	49·37	33·38	17·25	12·77	99·82	166
21	50·71	32·50	16·79	13·02	99·32	165
22	52·81	31·27	15·92	13·11	7·65	167
23	54·92	30·06	15·02	13·45	2·63	173

'The product of No. 15 was treated by a solvent indicated to the author by Brönnert as acting upon nitrocelluloses below octonitrocellulose—viz. a solution of 4 parts calcium chloride in 100 parts alcohol of 95 p.ct. This solvent extracted in the cold about 10 p.ct., on boiling with reflux cooler another 35 p.ct., but the remaining product contained almost exactly as much nitrogen as the original product, viz. 9·32 p.ct.' (hexanitrocellulose=9·17 p.ct. N).

The product of No. 20 has the exact composition of decanitrocellulose, and was perfectly soluble in ether-alcohol.

It is therefore evident that the decanitrocellulose exists in a variety of forms, soluble and insoluble. In reference to this point, it is to be noted that from the product of No. 21 to that of No. 22 there is a fall of solubility from 99·5 to 7·6 p.ct., determined by a slight variation in the composition of the nitrating mixture. In further discussing this question of the relation of solubility in 'neutral' solvents to composition, it is pointed out that a series of nitrocelluloses soluble in alcohol only result from the action of pure nitric acid on cellulose. Those obtained by the authors were of the composition of octonitrocellulose (11·0 to 11·16 p.ct. N). The products resulting from the mixtures of H_2SO_4 and HNO_3 at 1 : 1 with 15 to 20 parts water, though insoluble in alcohol of 95 p.ct., are soluble in absolute alcohol. Solubility in the latter, however, rapidly decreases with increase of nitrogen; and 'the true decanitrocellulose,' which is perfectly soluble in ether-alcohol, yields only 1·3 p.ct. to absolute alcohol. Experiments in varying the proportion of ether to alcohol showed that the solvent action of the mixture persists through wide variations from the usual proportion of 3 : 1.

In reference to the supposed correlation between nitrogen percentage and solubilities, Kisniemsky has endeavoured to reduce this to mathematical expression (Mém. des poudres, 10, 64) based upon the experiments of Bruley (*loc. cit.*). The author considers that, in view of the experimental results now recorded, the attempt is *à priori* hopeless, and he has found that the indications derived from Kisniemsky's formula are quite uncertain and in many cases directly misleading.

The paper contains the results of a careful investigation of several subsidiary questions, of which we note:

1. The alleged influence of the lower oxides of nitrogen in

the acid mixture on the composition and proportion of nitro-celluloses resulting from its action: The experiments in elucidation of this point consisted in reproducing the results with known mixtures, to which was added N_2O_4 in known proportions, from 0·13 to 9·28 per 100 of nitrating acid. The results are summed up in the statement that nitrogen tetroxide in the nitric acid, even far beyond the proportion ever found in commercial acids, has no injurious action in the manufacture of gun-cotton, neither in nitrogen percentage, yield, nor stability, as measured by the ordinary test.

2. The formation of 'oxycellulose' in the nitrating process: To detect and also to arrive at an approximate proportionate measure of oxycelluloses in the nitrated products, the latter were digested for 1 hour at 100° in a standardised solution of methylene blue, and the amounts of colouring matter fixed per 1 grm. of nitrocellulose were estimated as follows:

Nitrogen in nitrocellulose, p.ct.	Methylene blue fixed by 1 grm. nitrocellulose
0·0 (original cellulose)	0·0012
13·65	0·0010
13·21	0·0009
12·76	0·0011
12·05	0·0021
10·93	0·0036
8·40	0·0120

From these results it is concluded that oxycelluloses are formed under the action of the more dilute acid mixtures.

3. The behaviour of different commercial grades of cotton in nitration: This point was considered chiefly in regard to the production of collodion cotton. 'Authentic samples of cottons of the most divergent grades were carefully cleaned mechanically and washed in the same way as in the preparation for the manufacture of gun-cotton.' They were nitrated under uniform conditions with the same acid mixture (H_2SO_4

63·84 p.ct., HNO_3 16·96 p.ct., H_2O 19·20 p.ct.), with the following results :

No.	Commercial designation	Nitrogen, p.ct.	Solubility in ether-alcohol, p.ct.	Yield, p.ct.
1	Chemically pure surgical cotton-wool	11·76	100	159
2	American cotton 'middling fair' .	11·56	100	157
3	American cotton 'Florida' . .	11·67	100	153
4	Egyptian cotton, white, 'Abassi' .	11·69	100	155
5	Egyptian cotton, natural yellow .	11·61	100	154

It is concluded from these results that variations in 'commercial' quality are without influence on the behaviour of cotton as a chemical individual in the nitrating process.

* * * * * * *

Upon this communication we make the following comments :

1. The experimental numbers cover an extensive range, and, apart from considerations drawn from the personal reputation of the author, they present, on the internal evidence of the communication, a degree of cohesion and accuracy, both reasoned and objective, which entitles us to deduce a conclusion which otherwise would not be warranted. This conclusion is a momentous one in relation to the general argument in Chapter I., p. 5, and we state it in its simplest terms. The stages of nitration of cellulose are not molecular stages, but represent progressive increments of the esterifying groups in a mass-aggregate, which is the reacting unit. If the experimental data are carefully analysed, it will be seen that the number of coincidences with molecular proportions, on the assumed C_{24} dimensions of the cellulose molecule, are not more conspicuous than the divergences, to meet which we should now require to at least double these dimensions. We need not consider the numbers in detail, which would be merely to reproduce the substance of the paper, but we may take one series as especially illustrative, viz. that in which the effect of the higher tempera-

tures—40°, 60°, 80°—in the nitration process are investigated (p. 37). The series of products obtained under this range of variations, which were seven in number, show a nearly constant nitrogen percentage, 13·07–13·12, intermediate between the deca- and endecanitrocelluloses (the exact mean being 13·14 p.ct. N), at the same time that the yield of product falls progressively from the theoretical, with the first of the series, to 50 p.ct. of the theoretical with the last. Every circumstance of the original reactions points to an end-product and, even after the fractionation attending the prolonged action at 80°, there is no change of composition.

So far therefore as experimental numbers can establish the point, it would be necessary to admit a definite constant between the stages of the deca- and endecanitrocelluloses; in other words, to adopt a molecule of n.C_{48} dimensions in order to formulate the ester in question without employing fractional ratios. Instances of this order can be multiplied to show that the progress of research in this series of esters is obviously rendering 'the cellulose molecule' a *function* of the degree of refinement of experimental observations. The question arises, Is it necessary to retain this variable, if not elusive, quantity? We have already indicated reasons for taking another view of the reacting unit, and we shall return to the question.

For the purposes of a general survey of the series of nitric esters, we suggest the following statistical method of expressing their quantitative relations: we may admit as experimentally established that the limit of nitration is the nitrate with 14·14 p.ct. N. If we assign to this limit the convenient percentage limit, viz. 100, and express the lower esters by corresponding numbers, i.e. as percentages of this maximum, we shall have a nomenclature free from any objection. Since also $\frac{100}{14 \cdot 14} = 7 \cdot 07$, the approximate position of a given product is seen by multiplying the nitrogen percentage by 7.

2. A striking point in the series of experimental numbers is the suddenness of the transitions in the associated property of solubility (ether-alcohol), which are determined by

variations, relatively minute, of the percentage of water in the nitrating mixture. Thus in the series of p. 40, by increasing the water from 15·9 to 18·45, the solubility jumps from 3·2 to 98·7. In the series of p. 36 there are two transitions noted, the increase of water from 14·5 to 16·6, causing the solubility to rise from 22 to 99 p.ct.; and conversely, as the water increases from 20·26 to 33·50, the solubility falls from 99·8 to 1·15 p.ct. This was a series of experiments in which all other conditions were maintained 'practically constant, and only the proportion of water was varied.'

The evidence of these transitions is in favour of a reacting unit varying with the condition of the reaction. There is evidently a critical phase as regards the variant under consideration, which is at the proportion of from 15 to 22·5 of water p.ct. on the acid mixture. This phase is also coincident with structural changes in the fibre under nitration. It must be remembered that similar critical phases are met with in many other of the characteristic reactions of cellulose. These phases have their parallel rather in the behaviour of solutions; and are not consistently interpreted, on the ordinary view of reactions, as taking place between molecular reacting units considered as detached from one another and from the mass-aggregate in which they are associated. If we regard cellulose as a solution-aggregate of units which may be of lesser dimension than 'molecules'—ions, in fact—the configuration of the aggregate would vary with every change of equilibrium with external conditions.

The diminished avidity of the more dilute nitrating acid for the water split off in the reaction will permit an increased play of interior hydrolytic changes, and as a result the entire aggregate assumes a different configuration, with no essential variation in the stoichiometrical proportions which govern the reaction.

Returning to the experimental facts, it is evident that the author has given positive indications for the study of these phenomena, and the investigation of the products formed at these critical phases must throw a particular light on the funda-

mental problem. It would be necessary to examine these products, so as to fix more exactly their relationships, and to extend the investigation to the celluloses obtained from them by denitration.

3. The author introduces at more than one place the consideration of the lower esters, but the mention of them is only incidental. In view of a theory of cellulose constitution and reactions involved in a general theory of the colloidal state, it *may* be shown that the lowest numbers of the series have special significance; but this scientific interest is overborne by the fact that they have no 'useful'—i.e. industrial—applications.

The particular methods applied by the author to their examination are not described; but by implication it appears that, under treatment with the sodium ethylate reagent, nitrates containing 1·5 to 2·15 p.ct. N gave 40 p.ct. of water-soluble products of the saponification—in other words, they are stated to contain '60 p.ct. of unchanged cellulose.'

If we admit for the moment that these products are mixtures —viz. of di- or trinitrocellulose (C_{24}) with unchanged cellulose —it appears that these lowest terms of the series, which moreover cannot be formulated on the basis of molecular dimensions lower than C_{12}, are attacked similarly to the higher nitrate. We note this point as evidence against constitutional formulæ of C_6 dimensions, such as have been recently proposed (p. 133).

But there is an alternative to the author's conclusions which does not appear to have been considered—that is, that the mixtures, if such they be, are in effect homogeneous, representing a solid solution of the esterified groups in the cellulose-aggregate, the properties of which are modified as the properties of a solution would be. This alternative view is adopted, by implication if not in terms, in another publication which we have to notice, and we shall revert hereafter to its consideration. We may add before concluding these observations on the extremely valuable contribution of Professor Lunge, that we have suggested to him, in correspondence, the hypothesis of the 'continuous' esterification of the cellulose-

aggregate as an alternative interpretation to that based upon the conception of purely molecular constituent units. The *main objection* raised by the author is contained in words which we may be allowed to quote : 'It will require very strong evidence to convince me of such a contradiction to all our ordinary chemical *notions* as a continuous nitration *involves*. Hitherto I see absolutely no evidence against the natural view that the nitrocelluloses as practically obtained are mixtures of various stages of definite chemical compounds.'

It would be necessary to admit the force of this contention so far as regards any experimental mass of cellulose. Such a mass is made up in the first place of individual fibres, and these are essentially variable. Again, the individual fibres may be resolved into lesser masses, which may be regarded as structural components. The reacting unit we have in mind is of dimensions not necessarily those of such structural units, though definitely related to them; this conclusion being drawn from the intimate correlation of chemical and structural properties. We have to recognise that a reacting unit may be of variable dimensions and configuration, as, in fact, the solution of an electrolyte, between the terminals of a current which it conducts, represents some virtually continuous chemical mass in which the 'molecules' have ceased to exist. As far as we can interpret the consensus of evidence in regard to the colloidal state, it involves some analogous condition of matter, and the properties of colloids exhibiting organised structure mark them out as extreme numbers of a series of infinitely varied and differentiated forms.

2.

A LABILE NITRATE OF CELLULOSE.

E. Knecht (Berl. Ber. 1904, 549).

This communication has an interest which is complementary to the preceding, dealing with the phenomena which attend the formation of the lowest nitrates.

The experimental observations of the author relate to the 'absorption' of nitric acid by cellulose from acids of progressive concentration, together with the accompanying structural changes in the fibre, as measured by the contraction of the cotton yarn which was the form of cellulose employed. The acid 'absorbed,' or rather 'retained,' by the cellulose was measured as such, after allowing the yarn—previously squeezed and pressed to remove the excess of adhering acid—to remain for some days in vacuo over freshly ignited quicklime. The product 'dried' in this way was resolved by water into cellulose and nitric acid, and the latter was titrated. The following series of numbers resulted :

Sp. gr. of acid	HNO_3 retained by the cellulose	Contraction of the yarn, p.ct.
1·100	3·0	1
1·200	3·7	1
1·300	3·8	1
1·325	7·1	1
1·350	7·4	1
1·375	7·5	1
1·380	10·8	2·5
1·400	27·3	10·0
1·415	35·8	13·0

An absorption or adsorption compound of the formula $C_6H_{10}O_5.HNO_3$ gives the weight ratio 100 : 38·8. The author regards a compound of this order, and so formulated, as the initial stage of the true ester reaction. This stage, it will be observed, is confined within a narrow range of variations in concentration of the acid. At the sp.gr. 1·415 the proportion of nitrogen actually combined was found to be 0·5 p.ct. of the cellulose, which was left for 2 minutes in contact with the acid and immediately washed off. When, however, the product was pressed off and 'dried' in vacuo under the conditions of the experiments above described, then washed and analysed,

it was found to contain 2·2 p.ct. combined nitrogen. This confirms the results of Lunge.

It is pointed out that the structural alterations which attend the action of these acids are analogous to those which occur under the action of alkaline hydrates (mercerisation), as indeed was observed by Francis (Chem. Soc. J., 47, 183). Further, that constitutional changes are indicated by the increased attraction of the product for atmospheric moisture, which is stated to be 4 p.ct. in excess of the normal for cotton fibre.

Lastly, it is suggested that a labile nitrate of this order might be formulated, on the assumption of the cycloketonic formula of Cross and Bevan, as $CH_2.(CHOH)_4.C{<}^{O.NO_2}_{OH}$.

* * * * * * *

Upon this communication we make the following observations:

The author has been impressed with the associated phenomena of the reactions, affecting the structure of the fibres, and their general resemblance to those of mercerisation. The contrast is a further illustration of the amphoteric constitution of the cellulose-aggregate. We also note the sensitiveness of the equilibrium of the aggregate in regard to small changes in the concentration of the acid reagents, in which respect also the analogy with the reactions of mercerisation is fully maintained. If the reaction is approached as a case of equilibrium between two solutions, one of which is the colloidal fibre-substance, a much more promising field for experiment is opened up than by endeavouring to establish fixed points characterised by molecular ratios.

No doubt the cellulose undergoes considerable modification under the reaction and it would be of interest to establish (1) whether any hydrolysis takes place or whether the hydration changes which obviously occur are merely the result or cause of interior rearrangement, without permanent fixation of

water; (2) Whether the cellulose, after washing, has reverted to its normal equilibrium or, as is more probable, shows a permanent change of reactivity. The author notes, in effect, the increased absorption of 'hygroscopic' moisture; this is probably correlated with increased activity in regard to absorption or adsorption combinations generally; lastly, there may be more profound changes, such as would modify the reactions of solution in aqueous solvents or of esterification.

This series of absorption reactions are obviously continuous with the ester reaction proper.

3 (*a*).

MIXED ESTERS OF CELLULOSE, AND THE INTERACTION OF CELLULOSE AND NITRATING ACID.

Ueber die Gemischten Ester der Cellulose und das Verhalten der Cellulose zur Nitrirsaeure.

C. F. Cross, E. J. Bevan, and R. L. Jenks (Berl. Ber. 1901, 34, 2496).

This is a continuation of researches on mixed esters, of which certain types were described in the previous volume ('Researches on Cellulose,' 1901, p. 39), notably the aceto-benzoates and nitro-benzoyl nitrates. In view of the well-defined reactions of both sulphuric and nitric acids with cellulose, it must be presumed that in presence of a mixture of the acids both will react with the OH groups of the cellulose. Those reactions might be simultaneous and independent, resulting in an equilibrium defined by their relative avidities, or the sulphuric acid might act as 'pioneer,' the SO_4H residue being progressively replaced by NO_3.

The experimental results described in this communication establish the fact of the production of mixed esters. They

show that in the case of a bleached cotton cellulose the proportion of SO_4H fixed is highest with the concentrated acid mixture (H_2SO_4 : HNO_3 = 3 : 1), and diminishes as the mixture is diluted with water. In the following series the duration of the nitration was 1 hour at 16°, and the products were washed for 10 to 15 hours, with successive changes of boiling water, till neutral:

Nitrating acid		Sulphuric acid in combination as mixed ester. As H_2SO_4 p.ct. of ester
Water, p.ct.	H_2SO_4 : HNO_3	
10·14	3 : 1	0·00
2·30	3 : 1	0·23
0·0	3 : 1	{ 0·83 1·00
0·0	3 : 1	1·35

In a second series the duration of nitration was limited to 7 minutes, and the products were washed with cold distilled water until neutral.

Nitrating acid		Yield of product	Sulphuric acid	
Water, p.ct.	H_2SO_4 : HNO_3		Product, p.ct.	Original cellulose, p.ct.
10·13	3 : 1	152·7	2·56	3·91
2·30	3 : 1	161·2	2·52	4·06
0·0	3 : 1	134·4	4·62	6·21

A series of observations on unbleached cotton gave results varying in the contrary direction; highest (4·17 p.ct. H_2SO_4) with the diluted mixture, and lower (1·89 p.ct. H_2SO_4) with the pure monohydrate mixture.

These results were sufficient to establish the fact that sulphuric acid takes part in the ester reaction, in addition to its dehydrating function; which effect has obviously to be taken into account as one of the causes of instability of the

cellulose nitrates, in the condition in which they are obtained when entirely freed by washing from the uncombined residues of the nitrating acid.

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3 (*b*).

ON THE FORMATION OF SULPHURIC ESTERS IN THE NITRATION OF CELLULOSE, AND THEIR INFLUENCE ON STABILITY.

C. W. HAKE and R. LEWIS (J. Soc. Chem. Ind. 1905, 24, 374, and 914).

These investigators were led by extensive observations on commercial gun-cottons and derivative products to infer the existence of a cause of instability 'not previously recognised.' They found generally a tendency to liberate sulphuric acid when placed in contact with water, and from the mode of its formation, progressively with successive washings and dryings of a particular gun-cotton, it was inferred that it must result from the hydrolysis of a sulphuric ester.

Direct experiments were then made, typical samples of purified cottons being nitrated under ordinary conditions, and afterwards subjected to prolonged washing till free from (soluble) sulphuric acid.

Fifteen samples thus prepared, and under varied conditions as regards the nitrating mixture, were analysed and found to contain sulphuric acid (SO_4H) in variable proportions, the limiting quantities being 0·22 to 0·79 p.ct. of the nitrocellulose. The results were confirmed by observations in which Swedish filter-paper was taken as the purest form of cellulose obtainable, and nitrated under standard conditions. In the fully washed nitrates, the combined H_2SO_4 was estimated and

found equal to 2 p.ct. of the weight. Various observations were then made to determine the conditions necessary for the elimination of the combined sulphuric acid. It was found to yield very slowly to the action of boiling water. Various acids were tried, but found to have no appreciable solvent action. It was found, however, that when the gun-cottons were slightly moistened (8 to 10 p.ct. water) and exposed to the vapour of acetic acid in a closed space at ordinary temperatures, the ester was attacked and, on subsequently washing with water, sulphuric acid was removed. The action is progressive and several treatments are necessary for the complete elimination of the sulphuric acid.

The vapour of nitric acid produces a similar effect, but the action is more rapid; one treatment for 48 hours effects the complete elimination of the sulphuric residues.

The authors consider that their results fully establish the presence of combined SO_4H residues in cellulose nitrates prepared with the ordinary acid mixture, and also that the conditions of the ordinary stabilising treatments coincide with those which might be presumed to be necessary for the selective saponification of the sulphuric ester groups.

In their second communication (*ibid.* p. 914) the authors state that, in the discussion which followed the reading of their paper, their attention was called to the earlier paper on the same subject (Cross and Bevan, Berl. Ber. 1901, *supra*) which, although a careful search was made, was entirely overlooked.

* * * * * * *

Upon these communications we may remark that we have found the study of the nitrocellulose sulphuric esters less promising than that of the aceto-sulphuric esters; and having in our original communication established the fundamental fact and pointed out its technical consequences, we have prosecuted the investigation by way of the group of analogous

mixed esters the preparation of which is easily controlled. A full account of these mixed esters is given on pp. 83–92.

A study of the saponification of these aceto-sulphates shows that the SO_4H residues are relatively resistant to alkaline reagents, from the fact that they combine with the saponifying alkali, unless previously existing in the form of salt (Ca, Mg, Zn). In either case, in saline form these residues are not readily attacked. This justifies the conclusions of Hake and Lewis, particularly confirmed by G. Macdonald in the discussion on their paper, that a more perfect and rapid stabilisation of nitrocelluloses is secured by keeping up an acid reaction in the waters during the boiling of the esters.

The elimination of these residues by exposure to nitric acid vapour is probably the result of esterfication by substitution of the monohydric acid. Generally, the substitution of SO_4H by NO_3 is characteristic of the nitrating process under the usual conditions. Conditions will, no doubt, be found under which this process may be controlled for more exhaustive investigation.

It would, of course, be a matter of considerable interest to determine whether these fractional residues of SO_4H groups are homogeneously distributed in the sense of modifying the properties of the nitrocellulose as a whole. On the 'molecular' view of cellulose—i.e. of its reacting unit—it would be generally held that these minute proportions merely represent the average composition of a mixture. For reasons previously given, we do not regard this as a necessary interpretation.

4

RESEARCHES ON THE STABILITY OF NITROCELLULOSE.

Untersuchungen ueber die Stabilitaet von Nitrocellulose.

W. WILL (Mittheilungen: Neubabelsberg, 2, 1901, and 3, 1902)

These important communications are already well known, and have, in fact, procured a general acceptance by specialists of the experimental methods which they describe, as well as of the conclusions which the author draws as to the measure and definition of stability of a given nitrocellulose.

It has long been known that, at temperatures considerably below the explosion point, the nitrocelluloses are gradually decomposed with evolution of nitric oxide. To measure the amount of nitrogen thus given off the author devised an apparatus and an experimental method which provides that the nitrogen oxides are carried forward, in a stream of inert gas, over ignited metallic copper, by which they are decomposed, and the resulting nitrogen (together with any nitrogen possibly formed as an original product of decomposition of the nitrocellulose) measured.

The first communication leads to the general conclusion that 'the best definition and test of a stable nitrocellulose is that it should give off at a high temperature equal quantities of nitrogen in equal times.'

This is based on the results of an extended experimental investigation in which the test in question is applied to fix the relation of stability to the several essential factors both of the process of nitration and the various methods of after-treatment usually employed to correct the defect of instability which always characterises the original nitrate. The method enables the operator to follow the progress towards the stable condition attained under the usual treatment of prolonged boiling,

or by any alternative process; this 'stable condition' becomes, therefore, a 'limiting condition' (Grenzzustand) or a definite property of the nitrate, and it represents, in fact, its *normal instability*. For a full account of these investigations we must refer the student to the original paper, or to the abstract in the J. Soc. Chem. Ind. 1901.

In the second communication the subject is pursued in reference to the wider and more scientific bearings of the results. In the first section it is more clearly emphasised that the 'limiting equilibrium' measured in terms of the test is a fundamental property of the nitrate, and the test therefore eliminates all the disturbing factors which may cause variable effects in the methods of testing previously current.

In the second section is considered the question of the minimum evolution of nitrogen, which is an invariable for a given nitrocellulose once stabilised, but varies for nitrocellulose produced under varying conditions.

Thus, in a series of nitrates produced by acid mixtures in which the ratio $H_2SO_4 : HNO_3$ was constant—viz. 3 : 1—but the water was varied in the percentage proportions 4, 9, 14, the test applied by the several products showed the following quantities of nitrogen evolved in each successive interval of 15 minutes:

Nitrogen	0·62	0·56	0·35
Acid mixture used in preparation	$4\frac{3}{1}$	$9\frac{3}{1}$	$14\frac{3}{1}$

With still further dilution of the nitrating acid and reduction of the sulphuric acid (viz. under conditions of nitration represented by the formula $19\frac{1}{1}$), the N evolution of the stabilised nitrate was further reduced to 0·16. And moreover the stabilisation of this series of gun-cottons by the usual processes of washing and boiling exhibited a graduated facility proportional to the reduction of the N-constant.

It is then shown that the stabilisation is effected by various alternative treatments with water and with alcohol, both at the ordinary boiling temperatures and at 125° to 144°, without affecting the N-constant for a particular product; further, that when a product is fractionated by suspension in and deposition from water, and the fractions successively tested, the N-constant remains unvariable.

It has previously been shown that the N-constant—i.e. speed of decomposition—is not definitely related (1) to the actual nitrogen contents of the nitrate, (2) to its solubility in ether-alcohol, or (3) to the physical properties, chiefly viscosity, of its solution.

The evidence for the author's definition of the 'Grenzzustand' as the most characteristic property of a given nitrate is thus complete.

The question of the change from the unstable to the stable condition is discussed in reference to the main cause, which is held to be the elimination of secondary products which act as accelerators of the decomposition under the conditions of the stability test. In addition to the ordinary process of boiling with successive quantities of water, and the special treatments with particular solvents—solvents of the by-products—it is noted in certain cases that, after treating for some time at 135° under the conditions of the stability test and removal of acid products of the decomposition by washing with water, the N-constant falls to the minimum for the product under observation. With certain types of nitrates, on the other hand, the N-constant is unaffected by the treatment. Observations were also made in which the *addition* of reagents—e.g. $KMnO_4$, $KClO_4$—had the effect of reducing the speed of decomposition to the normal minimum. No definite conclusions, however, are stated as to the nature of these secondary influences, nor, more generally, the cause of instability in terms of the normal.

The probable influence of '*surface*'—i.e. the surface of the nitrates—is incidentally discussed in reference to the action of particular solvents which, whilst undoubtedly removing the by-product causing instability, also affect more or less the surface of the nitrate by the effect of partial gelatinisation. The actual influence of such structural change on the speed of decomposition—i.e. the stability test—is referred to further investigation. It is remarked, however, generally that the striking uniformity of the decomposition over a prolonged period of heating is conditioned by the peculiar structure of the cellulose (maintained in the nitrate) which allows large changes in weight, such as attend the decompositon, with no proportional change of surface.

The section concludes with a general statement on the technically important question whether stability, as previously defined in terms of the test, should be further limited to express the condition of the *lowest* attainable minimum speed of decomposition? The evidence has shown that in 90 p.ct. of cases investigated the ordinary process of stabilisation leads to a condition of the nitrate in which the 'Grenzzustand' coincides with this lowest attainable minimum. Of the remainder it cannot be said that there is any collateral evidence of non-fulfilment of any of the essential conditions of their employment as explosives. The definition is therefore maintained as sufficient on all technical grounds. The scientific fact however remains, that the normal instability is expressible in the two ways—i.e. in reference (1) to the *uniformity* of the decomposition over a lengthened period by heating; and (2) to the absolute amount of nitrogen lost in the successive unit periods.

The speed of decomposition considered in relation to the nitrogen contents of the series of nitrates leads to the general conclusion that with increase of nitrogen up to a nitrate of

9 p.ct. nitrogen, the speed of decomposition increases in simple proportion. From 9 to 13·5 p.ct. the 'normal instability' increases at a relatively higher rate, and at 13·5 p.ct. it is double that which would be calculated from the series of lower nitrates. This relation of divergence has also been found to hold when the temperature of observation in the stability test is raised to 145° and to 155°.

The speed of decomposition as a function of the temperature determining the decomposition leads to some important conclusions. As an example of the relations empirically established, the following tables may be cited:

(*a*) For a nitrate of 13·1 p.ct. N prepared with an acid of formula $9\frac{3}{1}$:—

Temperature	Speed of N evolution, mgr. per 15 mins.	Quotient for 5°
130	0·25	—
135	0·55	2·2
140	1·10	2·0
145	2·20	2·0
150	4·15	1·9
155	8·10	1·9

i.e. the speed of decomposition is doubled by each successive 5° of increase of temperature. A further development of this observed uniformity is seen in the following table of results obtained, (*b*) With nitrates lower in the series:

Temperature	N percentage of nitrate			
	9·73		7·35	
	N evolution	Quotient for 5°	N evolution	Quotient for 5°
135	0·35	—	0·13	—
140	0·68	1·9	0·25	1·9
145	1·27	1·9	0·50	2·0
150	2·55	2·0	1·05	2·1
155	4·90	1·9	2·05	2·0
160	9·95	1·9	3·95	1·9

The identity of the ratio $\frac{Nt+5}{Nt}$ over an extended series of cellulose nitrates is a further evidence of the invariable characteristics of 'stability' or the normal instability of these products. It is equally clear that the normal instability, measured in terms of this test, is the correlative of the ultimate constitution of these esters.

The ratio of N evolution to temperature is expressed by the equation

$$\log N = a + b \,.\, 0{\cdot}9932^t$$

in which N = the nitrogen evolved in unit time

t = temperature in ° Cent.;

a and *b* are constants, the value of which have been determined from the results of observations at 145° and 157° Cent.;

$$a = 8{\cdot}84211\ ;\ b = -22{,}857$$

0·9932 is a factor which makes the interpolation formula uniform with that applied by Barboli and Stracciati to express the relations of vapour tensions to temperature (Handb. d. Phys. II. 2, 733, Winkelmann). It is noteworthy that the same formula has been applied to express the dissociation tension of solid ammonium chloride as a function of temperature (Berl. Ber. 2, 139, Horstmann).

In the last section the author deals with observations specially carried out to supply data for an equation of the decomposition of the ester.

A quantity of 10·0 grms. of a given nitrate was heated at 135° in successive periods of 7 hours, until the weight of the residue was constant. The total duration of the heating was 371 hours, the final residue weighing 3·3 grms. and giving the following results of elementary analysis:

		Calc. for $C_{10}H_3NO_8$
C	44·4	45·3
H	2·4	1·1
N	5·3	5·3

The formula is calculated approximately to permit of a simple expression of the decomposition by the equation:

$$C_{12}H_{15}(NO_2)_5O_{10}=C_{10}H_3NO_8+4NO+6H_2O+2CO,$$

which is in accordance with direct determinations of the water given off and the ratio of the N evolution to the total loss of weight. The equation, however, cannot be regarded as finally established, and indeed the author's experiments go to show that N and CO_2 are simultaneously evolved, and probably also N_2O.

* * * * * * *

In commenting upon these important contributions we must avoid as far as possible anticipating the results of future developments on the lines of investigation which the author and his collaborators have initiated.

The question of the actual causes of instability of the cellulose nitrates—that is, the particular instability which has long been recognised as merely incidental, and as corrected by the ordinary processes of purification—is, of course, only a side issue of the broader question of the essential or normal instability of those esters. But in view of its technical importance and probable influence on the fundamental facts of constitution, it would be a serious omission in future investigations not to take into account the presence of sulphuric residues in the esters as originally prepared. This having now been fully established, together with the fact that the sulphuric acid in the ordinary acid mixture employed plays a direct part in the original reaction, it will be necessary to reconsider the question of stabilisation (1) in reference to the influence of SO_4 residues in the ester; (2) as to whether other incidental by-products contribute; and (3) whether there may not be some more fundamental factor involved, bound up with the actual constitution or configuration of the ester complex. There is a suggestion of the influence of this third factor in the investigations under discussion. In

one of the tables (2, p. 10) the minimum N evolution is shown to fall from 0·6 to 0·17, as the water in the nitrating mixture employed in preparing the ester increases from 4 to 19 p.ct. But further, whereas the ester prepared with the most dilute acid appears to have been stabilised by merely washing, the others were boiled for 70 to 120 hours in order to arrive at the 'Grenzzustand.' In our own researches, described on p. 52, it was shown that the proportion of sulphuric acid found in the ester reaction was a maximum when an anhydrous acid mixture was employed; on the other hand, with an acid of formula $10\frac{4}{1}$, we obtained an ester which was free from SO_4. In the exceptional case noted by Will, therefore, these later results afford an explanation of the direct production of a stable nitrate. But for the low minimum of N evolution in the 'Grenzzustand' we have to find an explanation. It will be noted that the conditions of nitration in the exceptional case are precisely those in respect of which Lunge says 'at 18 p.ct. water the fibres appear somewhat contracted, and the characteristic twist of cotton fibre is lost.' It is also at or about this point of dilution that sudden changes occur in the physical properties of the nitrates, notably in the solubility in ether-alcohol. It is a coincidence which cannot be overlooked, even though the experimental results recorded by either observer are not numerous. Lunge and other observers have fully established the fact that identity of empirical composition, with the associated factor of yield of nitrate, is compatible with considerable divergence in physical properties of these esters; and to this divergence we have to add the variation in normal instability, independently of the secondary instability due to SO_4 residues—i.e. to mixed ester groups, or to by-products of the reaction. This variation is of greater significance since it is an expression of a more obviously chemical property and of its variations. If we consider the actual reacting units, it would be generally admitted that the typical ester reaction $X.OH + HNO_3 = H_2O + X.O.NO_2$ can only take one invariable course. It might be admitted that, in the successive esterification of five OH groups in the C_{12} 'unit,'

there would be a gradation in stability of the combination of the negative groups in the resulting ester; but for the moment we are dealing with the marked variation in stability of types of identical degrees of esterification. The conclusion to be drawn is that the cellulose complex is a variable, under the varying conditions of nitration; that it may assume a configuration in which the OH groups are more basic than in another. Of this, in fact, we have numerous instances in other reactions of cellulose. If this is the true significance of Will's measure of normal instability, it can be verified in more than one independent direction of investigation. Not only can the types showing divergent instability be specially investigated in regard to correlative properties, but other nitrates can be submitted to the dissociation test, more especially a series of metallic nitrates, the elements being selected on the basis of variations of valency and chemical function.

But if such variations of normal instability are striking, equally so is the uniformity of the results of the stability test in the majority of cases recorded by Will. Unfortunately, perhaps, the technical objective of the investigation has prevented the simultaneous extension of the inquiry to the more fundamental elements of the problems involved—through the investigation of which the actual mechanism of the decomposition would be revealed. The author certainly suggests that the decomposition is primarily one of simple dissociation; and the attendant oxidations of the carbohydrate nucleus are secondary phenomena.

On this view it would be important to measure the factor of *surface*, and this can easily be accomplished by taking the nitrates in the form of continuous regular threads of definite dimensions. Next, it would be important to ascertain whether any condition is involved comparable with the osmotic penetration of 'hygroscopic' moisture from the surface of cellulose masses to the interior, and *vice versâ* under desiccating conditions—whether, to state the point more exactly, the liberation of the NO residues takes place only at the limiting surface, and is preceded by actual migration of the negative groups

within the mass of the ester. If the decomposition under heat is an exact reversal of the esterification process, we should assume a mechanism of this order. In any case, the experimental study of both groups of phenomena leads to the conclusion that they are progressive and continuous, and suggests that we are dealing with a reacting mass of indefinite dimensions rather than with an assemblage of individual molecules.

Will has, no doubt with intention, avoided the discussion of these fundamental questions, as the introduction of controversial points would tend to obscure the obviously main purpose of his contributions, which is to establish an experimental method. He therefore adopts the molecular interpretation of the reactions, and for the sake of simplicity and empirical directness the C_{12} unit.

But the very essence of this new departure is that it introduces a dynamic method of observation, and is a complete break with methods of investigation involving only ultimate analytical data and ratios.

The same feature we have found to mark the later investigations of the esterification process; and although in this case also the authors endeavour to find a complete expression of their results in interpreting them on the basis of molecular relations, there is evidence to show that these are inadequate and that the phenomena involved are progressive and continuous.

The line of progress is thus clearly marked out in attacking cases where the individual peculiarities of cellulose assert themselves more and more: recognising from the strictly objective standpoint that the only fixed ratios are the stoichiometrical equivalents of the ultimate reacting groups, these reacting groups being associated in a complex of indefinite dimensions and in such a way as to allow of reactions of synthesis and decomposition proceeding progressively and continuously—in which, therefore, molecular dimensions cannot be assigned to the complex or aggregate.

5.

SMOKELESS POWDER, NITROCELLULOSE, AND THEORY OF THE CELLULOSE MOLECULE

J. B. Bernadou (London, 1901, Chapman and Hall).

This is an essay of some two hundred pages, dealing in the main with problems connected with Service explosives; but from the title it may be gathered that the author travels outside the range of these technical questions to deal with the fundamental problem of the constitution of cellulose and the relation of the nitric esters to the parent 'molecule' or aggregate. The earlier chapters contain the original matter of the work, leading up to the exposition in Chapter IV. of a theory of the constitution of cellulose, of which we shall give a brief account. This is followed by a series of supplementary chapters (Appendix I.–IV., pp. 80–193), which contain the *author's translation* of well-known papers of Vieille, Bruley, and Mendeljeff on the nitric esters of cellulose, concluding with the reprint of a lecture delivered by himself in 1897 before the United States Naval War College, on 'The Development of Smokeless Powder.'

The 'theory of the cellulose molecule' is developed from a generalised view of the specific solvents both of cellulose and of its nitric esters—that is, of the causes underlying these particular solvent actions. The question was approached through a series of original observations on the solubility of nitrocellulose in ether and in alcohol, the results of which are summed up as follows:

1. 'Pyrocellulose' (the pyrocollodion of Mendeljeff) is readily dissolved in ether upon application of cold.

2. All soluble nitrocelluloses acted similarly in presence of an excess of ether, but some are more readily disintegrated by ether upon application of cold than others.

3. The necessary degree of cold being developed, soluble nitrocelluloses were not only soluble to any desired extent in ether, but could be colloided directly therein without recourse to liquefaction.

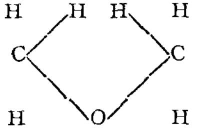
4. The addition of a few drops of alcohol in difficult cases appeared to be equivalent to a lowering of temperature—i.e. in increasing solubility.

It appears, therefore, generally that the nitrocelluloses are soluble both in ethyl ether and in alcohol at extremely low temperatures, whereas they readily dissolve at ordinary temperatures in mixtures of those liquids.

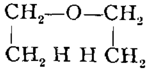
To account for these phenomena the author starts from the general view formulated by Cross and Bevan in reference to the actions of aqueous solvents—that is, that the amphoteric equilibrium of the cellulose-aggregate yields only to the simultaneous attack of both acid and basic groups in the solvents, the resulting solutions representing a species of colloidal double salt.

Both alcohol and ether, as well as cellulose and its derivative esters, are formulated to harmonise with this postulate. We reproduce the author's 'type forms':

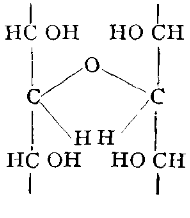
Ethyl alcohol.
C_2H_6O
[Under strain in methyl ether.]



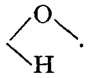
Ethyl ether.
$(C_2H_5)_2O$



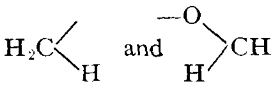
Cellulose.



This latter is termed the unit of polymerisation; and as the terminology employed is the author's own, we proceed to quote:

'From an examination of the unit of polymerisation it will be seen that the atoms of carbon are united (1) by single bonds with each other, (2) with hydrogen bonds, (3) with hydroxyl bonds, and (4) with what may be termed "water bonds" of the form . The free carbon bonds represent polymerisation; the hydroxyl radicles represent nitration in the mean and higher stages; the water radicles represent mercerisation, and nitration in the lower stage; the open oxygen bond in the 'water' radicle represents colloidisation by combination of the half-molecule of the nitrocellulose with the half-molecule of the solvent.'

And again: 'If alcohol is capable of effecting the solution of a nitrocellulose, it must effect the solution of both its components or resolve itself into two sub-components, each reacting on one sub-component of the nitrocellulose. These sub-compounds, in the case of alcohol, are



The molecule of cellulose should also be represented so as to permit a resolution of the original material into acid and basic sub-components through the disintegration of the water groups.

These postulates are applied to the experimental phenomena of (1) nitration, which is to be regarded as a progressive reaction attended by progressive changes of the reacting mass of cellulose, and (2) hydration.

'Since nitration starts, in accordance with our theory, in

nitro-substitution in the water radicles . . . the hydration should start in the rearrangement of the parts of the molecule adjacent to those water radicles. . . . As hydration proceeds, transformation advances towards the total conversion of all the water radicles into hydroxyl radicles. This is accompanied by disintegration of the fibre and a tendency to enter into solution. . . . The molecule splits into two halves, between which there is no chemical union . . . except such as may be represented by electrolytic strain.'

* * * * * * *

We have given a short account of this work so far as it aims to contribute to the main problem presented by the chemistry of cellulose. The author's views could not be accepted by chemists as a comprehensive statement of the elements of the problem of the constitution of cellulose, nor can we attach any value to the graphic constitutional formulæ employed to embody his conclusions, for these resolve themselves as regards cellulose into a hexahydric alcohol $C_6H_6(OH)_6$, and a view of the fully hydrolysed constituent molecules which is obviously inadmissible. We do not insist that a particular view of a complex subject is to be rejected because it is heterodox; but the heteroxody must be at least justified by an exhaustive examination of the antecedent orthodoxy. Since this is not in any way attempted, we cannot recommend this section of the author's views to the serious notice of students of the science. But this does not detract from the general value of the contribution, which lies in the perspective to which the treatment of the subject is subordinated. Thus 'cellulose' to the author is not merely a complex chemical individual, but represents the 'organic' influences under which it was produced. In other words, visible structure or external form are inseparably connected with ultimate configuration or chemical structure. The solution phenomena of cellulose and its derivatives are related to constitution in the chemical sense; also there is a complete external parallelism between the solution of the water-soluble

forms or derivatives in water and of the esters in their specific solvents, and the causes underlying the interaction between solvent and solute may be regarded as similar. Lastly, the resolved molecules of cellulose and the semi-molecules of the solvents, which are an important feature of the author's hypotheses and arguments, are in effect electrolytic antipodes or ions. These terms, however, are not employed, neither is there any reference in the author's exposition to the general theories of the colloidal state now current. We can only recognise therefore the definite but uncoordinated suggestions of a labile or plastic configuration of the complex, the mental picture of which is quite different from that of an aggregate of hexose molecules or polymeride.

As regards the remainder of the work, it is a most useful compilation, especially valuable as a contribution to the technology of explosives.

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6 (*a*).

ON THE WETTING OF COTTON BY WATER AND BY WATER VAPOUR.

O. MASSON (Proc. R. S., 1901, 74, 230).

The former of these papers (*a*) embodies the results of a close study of the thermal phenomena attending the absorption of moisture by cellulose. In a preliminary account of previous researches on this subject, the author overlooks the investigations of C. Beadle and O. W. Dahl (Chem. News, 1896, 73, 180,) whose results in terms of

$$\frac{\text{gain of weight}}{\text{time of exposure}} \text{ and } \frac{\text{rise of temperature}}{\text{time of exposure}}$$

expressed in curve form, are in generally close agreement with those of the present paper, and were also extended to various forms of cellulose, including the structureless variety obtained from the sulphocarbonate solution.

The investigations of Masson have been carried out by means of refined experimental methods, with the purpose of analysing the aggregate phenomena in terms of their essential factors.

The thermal changes were measured as a rise of temperature of thermometers carrying the particular mass of cotton under observation wound tightly round the bulb and covering also a portion of the stem. The following remarks are made generally on the observations:

Ordinary cotton-wool, and the 'absorbent' modification, behave identically in saturated air; but when completely immersed in water the latter shows a relatively smaller thermal effect.

The rise of temperature reaches a maximum in 5 to 6 minutes on exposure to air saturated with aqueous vapour, 2 to 3 minutes in the case of immersion in water. The author considers that the experiments have proved 'that in both cases the heat-production is due, at all events primarily, to the condensation of water vapour on the surface of the cotton fibres. On this point it is noted later in the paper, when discussing the experimental results, that the heat evolved per mgrm. of vapour absorbed is 0·57 cal., which is equal to the heat liberated by 1 mgrm. vapour at 25° condensed to form liquid water at 37°·7; these were the experimental conditions.

In this calculation the specific heat of cellulose is taken at 0°·336 (Fleury). 'The uncertainties involved in the calculation forbid any further conclusion than that already given, viz. that the heat of absorption by cotton is composed mainly of the heat by liquefaction of water.'

The author's further conclusions may also best be given in his own words; first, in regard to the similarity of the thermal effects under the condition of immersion in water: 'though the absorption of vapour cannot be observed, it must certainly

occur. . . . The air which adheres to each fibre and fills all interstices maintains that separation of water and cotton surfaces which is necessary for distillation to occur from one to the other.

'Two questions remain to be discussed, viz. the probable fate of the vapour after it has been condensed in the surface of the cotton, and the bearing of the conclusions here arrived at on the nature of the Pouillet effect in general.

'As to the first question there seems to be three possible views. One of these—the view that it becomes chemically combined to form definite hydrates of cellulose—may be quickly dismissed as there are no facts to support it, and as the evidence points to the absence of any definite limit to the action. . . . At the opposite extreme is the view that the condensed moisture forms and remains as a liquid film on the surface of the solid.'

In criticising this possibility the author makes an approximate calculation of the actual surface of a mass, *w*, of cotton on the assumption that the constitutent fibres are uniform cylinders of diameter 188×10^{-5} cm., the area being

$$4w \times 1{\cdot}525 \times 188 \times 10^{-5} = 1{,}395\ w\ \text{cm.}^{\square},$$

1·525 being taken as the sp.gr. of cellulose. With *w* grms of water deposited, or as in the case of a typical experiment 0·118 grm., upon a mass of cotton of 0·900 grm., the thickness of the film would be 15×10^{-5} cm.

Referring to a paper by G. J. Parks on 'The Thickness of a Liquid Film formed by Condensation at the Surface of a Solid' (Phil. Mag. 1903, p. 517), the above dimensions are considerably outside the superior limit deduced by Parks—viz. 80×10^{-6} cm. for the general case.

The author then proceeds to state the third hypothesis 'that the deposited moisture does not all remain as a mechanic-

ally adherent film on the surface of the cotton, but undergoes continuous osmotic diffusion into the substance of the fibre, and forms with it what may be regarded as a solid solution of cellulose and water.' This, on a general discussion of the experimental results, is found to afford a consistent explanation of the phenomena.

It may be explained that a considerable portion of this paper is devoted to the statement of the results of the experimental observation, their graphic representation by means of curves, both the absorption effect and the associated thermal effect being so treated; and lastly, the mathematical analysis of the resulting curves so as to establish the general relation of the temperature, time, and absorption values. These relationships, satisfactorily established as they are *inter se*, and affording evidence of the value of the author's methods of observation, are not applied to the elucidation of the actual mechanism of the interaction between the cellulose and water, and therefore will not be noticed at greater length. It is only necessary to make it evident that future investigations of the phenomena will be very much facilitated by the author's contribution both of experimental method and critical treatment of the subject-matter, for the due appreciation of which the original paper must be consulted.

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6 (*b*).

INVESTIGATION OF THE HYGROSCOPIC PROPERTIES OF NITROCELLULOSE.

W. WILL (Mittheilungen: Neu Babelsberg, November 1904.)

Untersuchungen ueber die Hygroskopizitaet von Nitrocellulose.

Cellulose.—This study of the cellulose nitrates in relation to 'hygroscopic moisture' necessarily introduces the parent

substance or original cellulose as a basis of comparison. The investigations herein described differ from those of Masson in being directed mainly to the relations of mass or weight, in limiting conditions of absorption.

In a preface dealing with the general question, the author adduces the evidence for regarding this property of attracting moisture from the air as a definitely chemical property of the celluloses. It represents or is associated with a fundamental property of the fibre-substance, or cellulose, independently of its surface and external form. (H. Kuhn, 'Die Baumwolle, ihre Kultur, Struktur und Verbreitung,' p. 130, A. Hartlebens Verlag, 1892; J. Wiesner, 'Die Rohstoffe des Pflanzenreichs,' 2, 179, Engelmann, Leipzig 1903; Cross and Bevan, 'Cellulose,' 1895, p. 4; Beadle and Dahl, Chem. News, 71, 1; 73, 180; C. O. Weber, Ztschr. angew. Chem. 1899, 416.) It has long been generally known that the nitrocelluloses exhibit a similar attraction for atmospheric moisture, though in lower and variable degrees, depending mainly upon the degree of nitration of the product; also that this property and its variations exert an important influence on the ballistic properties of propulsive powders of which these esters are the characteristic constituent. By the investigations of Beadle and Dahl (*loc. cit.*) it was first definitely shown that in a series of nitrates in which the proportion of ester groups was progressively increased, the proportion of 'normal hygroscopic moisture' decreased in inverse ratio. The multiplicity of observations to be found in the literature of explosives suggested the necessity of introducing standard methods of observation, and the following are now the normal conditions adopted at Neu Babelsberg:

The substance is desiccated in an ordinary drying oven, kept at the constant temperature of $40° \pm 1°$. It is then exposed to an atmosphere saturated with moisture at 25°, the temperature being maintained at $25° \pm 0{\cdot}5°$. At its satura-

tion-point the substance is weighed in balances contained in cases in which the same conditions of temperature and humidity are maintained. It is obvious that the resulting constants for hygroscopic moisture have no absolute significance, since both the celluloses and cellulose nitrates are not fully desiccated at 40°. But this temperature is fixed for the reason that the nitrates, and even unstable nitrates, may be safely dried at this temperature without fear of decomposition.

EXPERIMENTAL RESULTS.—Of these we reproduce a typical selection:

A cotton cellulose dried at 90°, at 70°, and at 40°, otherwise under the same conditions, showed the following relationships:

Temperature	90°	70°	40°
Constant weight	3·907	3·924	3·959
P.ct. increase at lower temperatures	—	0·43	1·33

A similar comparison of three raw materials gave the following numbers:

—	Hygroscopic moisture by drying at		
Temperature of previous drying	40°	70°	100°
American raw cotton	6·9	7·8	8·3
Same, converted into high nitrate	1·46	1·61	1·68
Same, converted into low nitrate	2·38	2·60	2·71

Observations were made upon the *rapidity of absorption* under the standard conditions above described. The curves obtained for cellulose and for nitrocelluloses confirm those figured by Masson for $\frac{d/\text{absorption}}{d/\text{time}}$, corresponding with a relatively rapid initial absorption, with an asymptotic approach to the time-axis. The absorption in the first hour exceeds

one-half the maximum, whereas there is still a measurable increase after 20 hours' exposure.

A comparison of a range of raw materials for maximum absorption gave the following numbers:

Raw cottons of various origins, all between	7·3 and 8·9 p.ct.
Other celluloses and fibrous raw materials:	
Purified cotton rags	6·4
Wood cellulose	6·7–7·0
Hemp	7·7
Jute	10·8

Observations were made on various *starches*, the numbers ranging from 10·6 to 11·4 p.ct., with the exception of potato-starch, which gave 14·1 to 16·0 p.ct.

The influence of various treatments of the celluloses incidental to ordinary processes of purification or preparation, gave the following results:

'*Beating*' in a paper-making 'Hollander' increases the absorption from 7·5 to 9·25 p.ct. (averages of four samples): *ether-extraction* to a still higher point—viz. 9·7 p.ct. It appears therefore that the normal moisture of a pure cellulose under these conditions is approximately 10 p.ct., and that the moisture complement is influenced by the presence of the residues of oil-wax constituents present in bleached cotton cellulose.

Dilute Acids.—Exposure to 2 p.ct. HCl or to 5 p.ct. H_2SO_4 in the cold reduces the absorption in the ratio $\frac{1·0–2·0}{7·5}$; this is also observed when the treatment with acid follows the ether extraction.

Dilute Alkalis at boiling temperature produce but slight alteration; the same holds for the influence of prolonged (50 hours) boiling with water.

The following series of determinations show the relative absorptions of various derivative products:

		P.ct.
Oxycellulose (Nastjukow)		5·9
'Acid cellulose' (Bumcke)		16·1
Cellulose acetate (Lederer)		4·7
,, ,, (Weber)		4·7
Lustracelluloses		
From nitrates denitrated with NH_4HS		12·6
From nitrates denitrated with Cu_2Cl_2		11·8
From highly viscous solution with Cu_2Cl_2		8·9
From non-viscous solution with Cu_2Cl_2		15·2
Celluloses from denitration by Cu_2Cl_2 from	Nitrocellulose 12·98 p.ct. N	8·2
	,, 11·54 ,,	8·5
	,, 11·52 ,,	9·1

Cellulose Nitrates.—A selected cotton was nitrated in portions under such conditions that a series of twelve products with N percentages varying from 8·5 to 13·15 was obtained; for which series the absorptions (1) corresponding to these extremes were determined at 6·16 and 1·42 p.ct., and (2) for the intermediate terms a series of intermediate figures such that the sum of the figures for

$$\text{Nitrogen percentage and absorption} = 14{\cdot}6 \pm 0{\cdot}1.$$

The observations were extended to nitrates prepared from a varied range of raw materials, for which this empirical constant was also found to hold good. So also for nitrates obtained by partial denitration of the higher nitrates. The constant was further found to be independent of the factor of solubility in ether-alcohol. Moreover, the *rapidity* of absorption was found to be uninfluenced by large differences in proportionate solubility.

A series of nitrates for which the constant had been determined as normal were dissolved in acetone and reprecipitated by pouring the solution into water. The corresponding structureless modifications retained their water-absorption capacity unaffected by the physical change. Nor was this affected by conversion into fully gelatinised flakes of 1 mm. □ dimensions.

The empirical constant thus fully established for all cellulose

nitrates lying within the range of technical usefulness—i.e. with from 8·5 to 13·9 p.ct. N—obviously fails to hold in the more extreme cases, since in one direction it would imply a *nitrate* with 14·6 p.ct. N, in the other a *cellulose* with 14·6 p.ct. hygroscopic moisture.

It remains to examine the series of constants in reference to the progressive substitution of the OH groups of the original cellulose (Beadle, *loc. cit.*; Cross and Bevan).

The progressive substitution of OH by ONO_2, in terms of

n=number of substituting groups,
M=molecular weight of nitrate,
N=nitrogen percentage,

involves the general expressions

$$N=100\frac{14n}{324+45\,n}$$

from which, by eliminating n,

$$M=\frac{10080}{31{\cdot}11-N} \quad . \quad . \quad . \quad (1)$$

Representing the values for M as a vertical ordinate and the corresponding values of H (hygroscopic moisture) as abscissæ we obtain a straight line expressing the relation

$$M+25{\cdot}07\ H=594 \quad . \quad . \quad . \quad (2)$$

and the new relationship H : N takes the form

$$H=\frac{334{\cdot}3-23{\cdot}65\ N}{31{\cdot}11-N} \quad . \quad . \quad . \quad (3)$$

whence the sum of nitrogen percentage and hygroscopic moisture is no longer constant. For the highest nitrate it has the value 14·14, reaches a maximum of 14·71 with a nitrate of 11·0 p.ct. N, and then falls to 10·78 with n=0, i.e. for the case of the original cellulose. Although such a number is in

excess of what may be taken as the normal for cotton cellulose, it lies within the range of the author's observed numbers for particular types of cellulose. It may therefore be concluded that the 'hygroscopic moisture' of the cellulose nitrates is inversely proportional to the number of ester groups. For the nitrates containing from 9·5 to 13·3 p.ct. N the empirical constant, N + H = 14·6 may be taken as representing the experimental facts.

Since the celluloses and the nitrates after drying at 40° C. show a further loss (0·3 to 2·0 p.ct.) when fully desiccated over sulphuric acid, it would be necessary in adopting this standard to change the constants in the above expressions (3) and (4) to the following:

$$M + 20{\cdot}71\ H = 594;\ H = \frac{405{\cdot}8 - 28{\cdot}7\ N}{31{\cdot}11 - N}.$$

On comparing the absorptions at lower temperatures, viz. at 15° and 5° with those at 25°, which has been adopted as a standard, the following numbers were obtained:—

Temperatures	N p.ct. of nitrate	Moisture absorbed
25° 15° 5°	13·20	1·42 2·75 3·00
25° 15° 5°	12·68	1·95 3·40 3·50
25° 15° 5°	12·06	2·43 4·30 4·61
25° 15° 5°	11·00	3·55 5·52 6·01
25° 15° 5°	9·87	4·74 7·35 8·10

The increased absorption at the lower temperatures does not change the general features of the process. The following are the corresponding empirical constants which obtain at these lower temperatures :

At 15° . . . $H = 20 - 1{\cdot}3\ N$
At 5° . . . $H = 21{\cdot}6 - 1{\cdot}4\ N$.

It is evident that the relationship between the humidity-equilibrium and temperature is not simple: it is probably complicated by interior hydration, or even hydrolytic changes in the cellulose complex itself.

Lastly the author has investigated the equilibrium as effected by varying the proportion of moisture in the atmosphere to which the nitrates are exposed.

The general result of the experimental results is to show that up to 80 p.ct. saturation the ratio of percentage absorption : percentage saturation of atmosphere, is approximately constant. A disproportionate increase in the former occurs as the saturation increases from 80 to 100 p.ct. This section of the subject is still under investigation.

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We comment on these two communications together for the reason that they are mutually complementary as to subject-matter. It will have been already noted that the authors arrive at opposite conclusions as to the causes underlying the common phenomena investigated. We associate ourselves rather with the views contained in Will's communication, confirming the conclusions which we have previously formulated ('Cellulose,' 1895, p. 4), while very much extending the area of observation. It will further be noted that Masson is chiefly concerned with the thermal phenomena involved, Will with the constants of weight equilibrium. It is superfluous to insist on the importance of the contribution of experimental method and results in either direction of inquiry. As to the mechanism

of the process, Masson distinguishes between the action at the surface of the fibres and the subsequent process of penetration of the interior mass of the fibre substance to form, as he states, a species of 'solid solution' with or in the cellulose. He also introduces the approximate calculation of the surface of a mass of cotton—incidentally to an argument disposing of the view that the moisture exists as a surface film (see p. 26).

With the 'artificial fibres' at command it should now be possible, by extending the investigations of both authors to these regular forms of the celluloses and cellulose esters, to estimate separately the influence of surface and osmotic penetration. Since these substances can also be produced in film form of any required dimensions, a very wide range of variations of surface to total mass can be controlled, and the investigation thereby much facilitated.

Reciprocally, from a more exact knowledge of these factors it may be possible to use the hygrometric observations as a measure of the actual surface of the 'natural' fibres.

Further, a more exact knowledge of the mechanical factors of the absorption will more clearly establish the chemical or molecular features of the limiting equilibrium. While these are generally emphasised by Will, and the final equilibrium is shown to be a property of the substances themselves, independently of their form or distribution in space, it is evident that this author was unaware of the investigations of Masson and his very opposite conclusions as to the causes, which require a more specific and particular refutation. Outside the question of the causes immediately involved and Masson's summary dismissal of the chemical interpretation of the phenomena, we suggest that a more comprehensive view of these effects will show that they cannot be separated from the general range of hydration-changes determined by alkalis, acids, and salts. The influence of the hygrometric state of the celluloses upon the mechanical properties of their aggregates is an evidence of the ntrinsic effects of the combined water; and it must be remembered that the structureless forms of cellulose are more sensitive than are the 'natural' fibrous forms, to these influences. It is

not superfluous to again insist on our contention that none of these problems can be adequately solved without the inclusion of these homogeneous, structureless modifications. The thermal effects noted and measured by Masson are similar in character, and also graduate without break into the effects of contact with dilute hydrolytic agents, acid and alkaline, measured by Vignon ('Cellulose,' 1895, p. 17). These are, no doubt, accompanied by volume changes, graduating into the more extreme effects produced by more concentrated reagents; and these correlations make a strong *à priori* case against Masson's interpretations, which present the phenomena as quite external to the cellulose. On *à priori* grounds, also, it is difficult to appreciate the motive for aqueous vapour at a lower temperature steadily migrating to a surface in order to assume the solid state at a higher temperature. It is true that Masson imports into his argument for this interpretation a numerical calculation from experimental data. But these data involve the 'specific heat of cellulose,' for which the doubtful number determined by Fleury (J. Chem. Soc. 1900, 2, 188) is taken.

While Masson fully recognises that the factor of the heat of liquefaction of water 'may be supplemented by some other process, either exothermic or endothermic,' which the experimental method employed could not test, he makes no suggestion that this process could involve constitutional changes in the cellulose substance. In Will's paper, on the other hand, the following passage occurs in discussing the influence of temperature on the hygrometric equilibrium: 'It is not impossible that in the circumstances (of absorption), there enter chemical changes in the molecule of cellulose (anhydride formation, hydrolysis of lactonic groups) which may be obscured by the apparently simple relationships between temperature and absorption.'

In conclusion, we are of opinion that the interpretations of these phenomena may be unnecessarily obscured by applying to them too exclusively the terminology of molecular compounds and the mental pictures which attach thereto. If, on

the other hand, we regard cellulose as a solution-aggregate in which the molecular forces are merged in new conditions, whether of dissociation or association; remembering, further, that these conditions have been originally imposed upon the cellulose under the conditions of complete hydration, and, in fact, solution in water; that the cellulose is both an anhydride by constitution and a dehydrated solution; that the process of dehydration has taken place under conditions of mechanical strain, which is made evident under 'mercerisation' and other processes of re-hydration, both by changes of volume and accompanying structural contortions—we have sufficient reason for asserting that the relationships of the celluloses generally to water are the expression of fundamental constitutional facts, which are equally the determining causes of their hygrometric equilibrium with atmospheric moisture.

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7 (*a*).

CELLULOSE ACETO-SULPHATES.

C. F. Cross, E. J. Bevan, and J. F. Briggs (Berl. Ber. 1905, p. 38 (A), p. 1859 (B)).

A. In the former paper the general preface connects the results to be described with those of a previous paper, in which the interaction of cellulose with a mixture of sulphuric and nitric acids was proved to result in the formation of mixed esters (Cross, Bevan, and Jenks, Berl. Ber., 34, 2496; see also p. 51). Owing to the difficulty of obtaining well-defined products in this series of mixed esters, the investigation was diverted into the more promising region of the aceto-sulphates, which had been found by preliminary experiments to be extremely well characterised derivatives. The method of preparation adopted was a variation of Lederer's process of acetylation, consisting in an increase in the proportion of sulphuric acid. The viscous

solutions which resulted from the reactions were poured into water, the products separating as gelatinous precipitates. These were washed till entirely free from acid. By varying the proportion of sulphuric acid added to the acetylising mixture—a mixture of glacial acetic acid and acetic anhydride in equal weights—it was found that the series of aceto-sulphates produced grouped themselves on divergent physical characteristics as follows:

Low series.—With 5·0 p.ct. combined SO_4, insoluble in alcohol, soluble in acetone.

Middle series.—With 8 to 9 p.ct. combined SO_4 soluble in hot dilute alcohol, the solution gelatinising on cooling.

Extreme series.—With 25 p.ct. combined SO_4, soluble in water, the solutions being highly colloidal.

The water-soluble series were only superficially examined; the lower series were treated by the methods usually adopted in separating and purifying the nitrates, similarly prepared, and were analysed, with results which generally established their relation to the original cellulose—viz. that on a C_6 unit three OH groups were replaced. The proportion of SO_4 in the middle series corresponded with a formula

$$4(C_6H_7O_2)SO_4(C_2H_3O_2)_{10},$$

which was also in agreement with the yield of product—viz. 174 per 100 of original cellulose.

In this preliminary research we observed certain anomalies in the behaviour of the products under treatment for purification—which, however, did not appear to influence the quantitative relationships of the substituting groups. On further investigation, however, we found that in the course of prolonged washing with water the products underwent changes: in the case of distilled water the esters became more and more

colloidal, but with an ordinary service-water containing 20/100,000 of $CaCO_3$ the change was arrested, and the product resumed its free washing characteristics.

These anomalies will be found to receive their explanation by the investigations recorded in the second communication, of which we give a full translation.

7 (*b*). B. In a recent 'Vorläufige Mittheilung' we have described a series of mixed esters resulting from the simultaneous action of sulphuric acid, acetic anhydride, and acetic acid on cellulose. Owing to the highly colloidal character of these derivatives their analytical investigation involves exceptional difficulty, and in our preliminary researches we became aware of certain variations in their products under preparation—changes in hydration capacity, and probably hydrolysis—which required explanation. The nature of these derivatives and the relationships of the series admits of more precise definition through the results of our continued investigation.

In order to avoid experimental difficulties arising from treatment with water, we varied the process of isolating the derivatives by pouring the 'Reaktions-gemisch' into amyl alcohol, and washing the precipitated product with this alcohol till free from sulphuric acid.

The products thus prepared could be dried at 100° C. without change, but they behaved, in contact with water or of alcohol, as free acids, and by quantitative observations the acidity was found to be approximately the equivalent of half the combined sulphuric acid.

Hence the inference that, at least in the presence of water, the sulphuric group of these esters takes the form of SO_4H.

This was confirmed by the preparation of the calcium, magnesium, and zinc compounds by pouring the product of

reaction into solutions of the acetates of these metals and washing with water till free from soluble impurities.

The analysis of these compounds or salts give numbers in satisfactorily equivalent ratios (*infra*).

It appeared therefore that the neutral compounds described in our previous communication were in effect the calcium salts of the acetyl cellulose sulphuric acid now described.

These products had been washed with a tap water containing 20/100,000 $CaCO_3$, and in the course of a somewhat prolonged washing they gradually took up the equivalent of basic matter.

A product so obtained and prepared as a film from alcoholic solution gave the following results on analysis :

Total sulphuric acid (H_2SO_4) . .	10·8 p.ct.
Total ash 6·5 p.ct., containing $CaSO_4$	5·9 ,,

which represents 40 p.ct. of the equivalent of the total SO_4 residue present as $\frac{SO_4Ca}{2}$.

The following brief statement of the later experimental results, while extending our previous results and modifying our conclusions as explained, will be found to confirm the more important data of our previous paper.

Preparation of Acetyl-cellulose Sulphuric Esters and their Salts.

In order to obtain more perfect esterification, it was found to be advantageous to increase the proportion of acetic anhydride to acetic acid from 1 : 1 to 2 : 1. The result of this variation was an alteration in the reaction equilibrium in the sense that a higher proportion of H_2SO_4 in the mixture was required to determine the same proportion of H_2SO_4 combining.

We may differentiate three well-marked terms of the series of mixed esters which appear to correspond within certain limits to definite stages of equilibrium.

(1) *Low series* (5 to 6 p.ct. combined H_2SO_4).—Cellulose was treated with 10 times its weight of a mixture of 2 parts of acetic anhydride, with 1 part glacial acetic acid, containing 4·25 p.ct. of H_2SO_4.

When the solution was perfectly clear the product of the reaction was divided into three portions and poured into

(*a*) Amyl alcohol,
(*b*) A solution of zinc acetate,
(*c*) A solution of magnesium acetate.

It was found necessary to employ amyl alcohol for the precipitation and washing of the product (*a*), since, when washed with distilled water, it cannot be dried without liberation of sulphuric acid, which, when heat is employed, manifests itself by charring the preparation.

The washing with the alcohol was continued for several days, until all traces of sulphuric acid were removed. The products (*b*) and (*c*) were washed with cold distilled water until the washings were neutral.

The product (*a*) of this series, after drying at 100° C. is a white amorphous powder, but in contact with water reacts as an acid ester or acetyl-cellulose sulphuric acid. On boiling with water it is gradually decomposed. It is freely soluble in acetone in the cold and in hot dilute alcohol. The acetone solution yields films of remarkable brilliancy and toughness.

The zinc, calcium, and magnesium salts are insoluble in boiling water and dilute alcohol, but they are soluble in acetone.

The calcium and magnesium salts are perfectly neutral bodies, and can be dried at 100° C. without change. The zinc

salt, probably on account of the peculiar acid function of the zinc, dissociates on drying even at ordinary temperatures with liberation of free sulphuric acid, and is completely charred when heated at 100° C.

(2) *Intermediate series* (the 'normal' products of our first paper (9 to 10 p.ct. combined H_2SO_4).—The ester itself and the zinc and magnesium salts were prepared under the conditions above described, but the higher proportion of combined sulphuric acid is conditioned by increasing the proportion of sulphuric acid in the acetylating mixture to 6·1 p.ct. H_2SO_4. In this case it is impossible to employ water in isolating the product (*a*), since it is gradually gelatinised and dissolved by distilled water, even in the cold. The salts (Ca, Mg, Zn) are resistant to cold water, and can be washed to a neutral reaction.

The product (*a*), which in this case also can be dried at 100° C. without change, is gelatinised by cold water, and is readily soluble in boiling water, the concentrated solutions becoming gelatinised on cooling; it is also soluble to some extent in cold strong alcohol, readily soluble in hot dilute alcohol and acetone.

The salts are also readily soluble in hot dilute alcohol, and the solutions gelatinise on cooling. The Ca and Mg salts are stable, and correspond with the products described as 'normal aceto-sulphates in our previous papers. The Zn salt dissociates on drying, and completely chars at 100° C.

High series, water-soluble (25 p.ct. combined H_2SO_4).—These products were made by treating cellulose with a mixture of equal parts of acetic anhydride and glacial acetic acid containing 15 p.ct. of sulphuric acid. The product of reaction was poured into water, in which it was perfectly soluble; the solution was filtered through cloth to remove residues of cellulose fibres, neutralised with caustic soda, and saturated with pure sodium chloride.

A precipitate was formed which coagulated when warmed to about 60° C., and which was then filtered off and washed with saturated brine at about 60° C. until the washings were free from sulphates.

The product was presumably the sodium salt of an acetyl-cellulose sulphuric acid. It could not be isolated in the pure state, but was pressed and dried, together with the sodium chloride, for the purpose of a preliminary analytical investigation. The percentage of cellulose compound was determined by burning with sulphuric acid, and deducting the NaCl equivalent of the ash from the dry weight. The results of these indirect analyses are given in the subjoined notes (Series 3).

This product was completely soluble in cold water, with which it formed a highly viscous, opalescent solution, resembling starch paste. It is particularly interesting as showing that we can proceed to high limits of esterification in this series without breaking down the cellulose aggregate, the nearest approximate formula being

$$C_6H_6O(SO_4H)(C_2H_3O_2)_3.$$

We are prosecuting the investigation of the series at these high limits so as to obtain derivatives which can be isolated in the pure state for direct analysis.

We may again point out that these investigations commenced with the study of the nitrates (*Berl.* Ber., 34, 2496), and the proof that, in the ordinary process of preparing the cellulose nitrates with a mixture of nitric and sulphuric acids, the latter acid reacts with the cellulose and SO_4 residues are fixed. We also indicated the bearings of this fact upon the important technical question of the stability of these esters. These observations have been fully confirmed and extended

by the later investigations of Hake and Lewis (J. Soc. Chem. Ind. 1905, 374, 914), see p. 53.

We are now sufficiently familiar with the group of aceto-sulphates to investigate mixed esters which contain, in addition, nitric groups. It appears that cellulose nitrates containing 12 to 13 p.ct. N are acted upon by the aceto-sulphuric mixture; and the resulting product is soluble in dilute alcohol. Moreover, the formation of the new product is attended by increase of weight, in spite of the displacement of a portion of the ONO_2 residue; it is probable that these derivatives contain acetyl, sulphuric, and nitric residues. We have therefore a new possibility of bringing the fourth O atom into synthetical reaction. It is clear that until the question of its function has been definitely resolved, we cannot usefully discuss the major question of the actual constitution of the cellulose complex. The production of a tetracetate[1] (C_6) is called in question in recent contributions, and, owing to the exceptional difficulty experienced in the analysis of these esters, the proofs of composition are lacking in cogency.

The solution of this problem is the ultimate aim of these investigations, and we reserve all further discussion until we have extended our investigations of the highest limits of esterification attainable under the conditions of reaction herein described.

We subjoin the results of analyses of typical preparations of aceto-sulphates of the three series described in this paper.

These preparations, which contained only traces of non-esterified cellulose, were not subjected intentionally to any process of fractionation with a view to separating different components. Their solubilities indicated that they were homogeneous substances, but the possibility of a certain

[1] A. G. Green in Ztschr. Farb. Textil. Ind., 3, 99, 309. See also *ibid.* 199 and p. 131.

amount of fractional dissolution or dissociation during the process of washing is not excluded.

Methods.—The hygroscopic moisture was determined by drying in the water-oven for 2 hours at 98° C. Since the zinc salts were charred by this treatment, their dry substance was calculated on the same basis as the magnesium salts. The total H_2SO_4 was determined after destruction of the cellulose by aqua regia, by precipitation as barium sulphate. The acetic acid was determined by neutralising the products with caustic soda in presence of phenol-phthalein, and then saponifying by a known excess of caustic soda in presence of 60 p.ct.

(1) *Low Series.*

—	Product (*a*) 'ester'	Product (*b*) zinc salt	Product (*c*) magnesium salt
	p.ct.	p.ct.	p.ct.
Normal hygroscopic moisture	7·5	decomposed	8·67
Total H_2SO_4	5·00	5·96	6·13
Percentage of total HSO reacting as acid to phenolphthalein	40·0	indefinite	nil
Mineral matter (ash) . .	0·80 (Fe_2O_3, &c.)	—	—
Zinc oxide as ZnO . .	—	1·93	—
Magnesia as MgO . .	—	—	1·02
Percentage of total H_2SO_4 saturated by ZnO or MgO respectively . . .	—	40·4	42·3
Acetic acid by saponification as CH_3COOH . . .	52·8	49·8	52·6
Saponified residue. (In this series the saponified residues are insoluble in dilute alcohol, and can be washed free from soluble salts) .	56·9	59·2	57·6
Containing ash sulphates .	4·5	4·30	7·6
Containing combined H_2SO_4	5·02	3·65	9·57
Percentage of total original H_2SO_4 remaining in combination in the saponified residue	57·0	35·0	93·0

alcohol. Saponification was allowed to proceed for 40 hours in the cold, and the alkali thus neutralised was calculated in terms of acetic acid, on the assumption that, after the neutralisation of any dissociated free sulphuric acid, the residual combined sulphuric acid is very nearly resistant to the saponifying action of alcoholic soda. Nevertheless, the values for acetic acid by saponification cannot pretend to any high degree of accuracy; they indicate however, in an approximate manner, the degree of esterification attained in these compounds.

(2) *Intermediate Series.*

—	Product (*a*) 'ester'	Product (*b*) zinc salt	Product (*c*) magnesium salt
	p.ct.	p.ct.	p.ct.
Normal hygroscopic moisture	12·6	decomposed	13·2
Total H_2SO_4	10·08	8·46	8·58
Percentage of total H_2SO_4 reacting as acid to phenol-phthalein	50·0	ndefinite*	nil
Mineral matter . . .	1·00 (Fe_2O_3, &c.)	—	—
Zinc oxide ZnO	—	3·36	—
Magnesia MgO	—	—	1·66
Percentage of total H_2SO_4 saturated by ZnO or MgO respectively	—	40·5	40·6
Acetic acid by saponification as CH_3COOH . . .	45·0	51·9	54·0

* The dry zinc salts contained varying quantities of dissociated free sulphuric acid, in addition to which the ZnO acted as an acid to phenol-phthalein.

Owing to the solubility of the saponified residue, even in 40 to 50 p.ct. alcohol, these products could not be washed without error, and consequently the combined H_2SO_4 in them could not be determined. The acetic acid value of the product (*a*) is probably too low, owing to the gelatinisation of this product by alcohol, and resulting difficulty of penetration

(3) *High Series.*

Two different preparations were analysed, giving the following results:

	Preparation 1	Preparation 2
	p.ct.	p.ct.
Percentage of cellulose compound present in the moist preparation = (dry weight − NaCl calc. from sulphate ash)	20·2	23·9
Normal hygroscopic moisture (calc. on cellulose compound)	—	17·8
Reaction	Neutral	Neutral
Combined H_2SO_4 (calc. on cellulose compound)	25·8	24·5
Acetic acid by saponification (calc. as CH_3COOH on cellulose compound)	49·2	29 8

8.

ON CELLULOSE-XANTHOGENIC ACID.

C. F. Cross and E. J. Bevan (Berl. Ber. 1901, 34, 1513).

Ueber die Cellulosexanthogensaeure.

In a previous publication (*ibid.* 26, 1090) the synthesis of the cellulose-xanthogenic acid was shown to consist of the two stages:

1. Interaction of cellulose and sodium hydrate in the molecular ratio $C_6H_{10}O_5$: 2NaOH.
2. Interaction of the alkali-cellulose with carbon disulphide in the ratio $C_6H_{10}O_5$: 2NaOH : CS_2.

The second molecule of NaOH is in direct combination with the cellulose, and the general empirical formula of the xanthate may be written $NaS.SC.O.C_6H_9O4.NaOH$. Direct evidence of the presence of OH groups of, relatively, acid function in

the cellulose residue, is afforded by the study of the series of those esters representing the several stages of spontaneous decomposition of the original product. In the later stages the ester compounds—i.e. the sodium salts—are insoluble in water, though freely soluble in presence of sodium hydrate.

Similar relations are brought out by the author's investigations of the interactions of the alkali cellulose and benzoyl chloride. When the reagents are brought together in the proportions

$$C_6H_{10}O_5 : 2{\cdot}0\text{–}2{\cdot}5\ NaOH : 1{\cdot}0\text{–}1{\cdot}5\ C_6H_5CO.Cl,$$

the monobenzoate (C_6) is produced without structural modification of the cellulose fibres. The yield is 80 to 85 p.ct. of the calculated proportion. To determine the maximum of esterification the reagents were brought together in the proportions prescribed by Skraup (Monatsh. 10, 389), viz.:

$$R(OH)_2 : 2[7NaOH : 5C_6H_5.COCl],$$

under which conditions the dibenzoate (C_6) is formed, the yield from the fibrous cellulose (cotton) being 90 p.ct. of the theoretical. Its formation is accompanied by structural changes, the dibenzoate being an amorphous product; and the structural continuity as between fibre and product, which characterises many of the ester reactions of cellulose, is in this case not maintained. It may be taken as proved that as a maximum proportion two OH groups in the C_6 units interact with the alkaline hydrate; and as regards the further reactions the same general conditions obtain in both directions of synthesis or esterification.

Further investigations of the xanthates have shown that the characteristic residue X.CS.S. is of stronger acid function than the monocarboxylic acids of the fatty series. Solutions of the xanthates (viscose) may therefore be acidified with these

acids—e.g. acetic acid in excess—without decomposing the typical group X.CS.S.Na. Since under these conditions the by-products of the reaction are entirely decomposed and the alkali converted into acetate, the observation has enabled the authors to devise simple analytical processes, by volumetric methods, for estimating the 'xanthate soda' in such solutions, and thus following the course of the spontaneous decompositions of viscose. This 'reversion' of the product to cellulose (hydrate) with progressive elimination of the CSS residues, particularly reveals the character of cellulose as a complex, the necessity of studying it as a complex, and therefore of introducing a statistical quantitative control of the analytical determinations, which are not required when dealing with simpler 'molecular' compounds.

The following are the analytical methods applicable to this series of compounds:

CELLULOSE may be determined in a weighed quantity of solution (viscose) by (*a*) 'coagulation' or precipitation by reagents, or by heat (*b*) spreading and drying down on a glass plate, washing in saturated salt solution, decomposing the xanthate with a mineral acid, washing, purifying, and drying the transparent *film*.

TOTAL ALKALI is determined by any of the ordinary methods.

XANTHATE ALKALI.—(*a*) After adding normal acetic acid in quantity equivalent to the total alkali, the xanthate (Na salt) is separated by neutral saturated brine (NaCl), and the uncombined acetic acid estimated in an aliquot portion of the filtrate from the xanthate.

(*b*) The xanthate may be titrated with $n/10$ sodium solution which attacks the xanthate according to the equation:

$$2CS{}^{O.R}_{SNa} + I_2 = CS<^{OR}_{S} \cdot {}^{R.O}_{S}>CS + 2NaI.$$

The numbers therefore for a pure xanthate are identical with those of titration with an N/10 acid (HCl, H_2SO_4).

TOTAL SULPHUR is determined by oxidising with excess of hypochlorite in alkaline solution, acidifying, filtering, and precipitating as $BaSO_4$.

As a result of analytical determinations by the above methods, the following typical characteristics are established:

(*a*)[1] *Original product.*—The reacting unit is approximately of C_6 dimensions, and the xanthate is soluble in, or at least is not precipitated by, neutral dehydrating agents. The aqueous solution, on standing for 24 hours under ordinary conditions of temperature, contains

(*b*)[1] *The* C_{12} *xanthate*, the characteristic constituent of an ordinary 'fresh' viscose. This body is precipitated by brine or alcohol.

(*c*)[1] *The* C_{24} *xanthate* is the stage reached in 4 to 5 days' progressive spontaneous change. It is the main constituent of a viscose approaching the point of solidification, and is in fact insoluble in feebly saline solutions.

(*d*)[1] *The later stages* are marked by complete insolubility in water; but the presence of residues of the typical xanthic groups determines solubility in solutions of alkaline hydrate; with closer approximation to the condition of cellulose, the products require increasing concentration of the alkali for complete solution.

The analytical results do not allow the affirmation that there are actual breaks in the continuity of the spontaneous decomposition; especially when it is remembered that the actual analytical operations involve new conditions of equilibrium, which may induce decompositions. The stages above described are therefore to be regarded as transition-phases,

[1] These represent stoichiometrical ratios.

within which the xanthates have the particular 'physical' characteristics which have been noted.

* * * * * * *

As an appendix to the above communication it may be recorded that the accumulation of experience in the application of these methods confirms their general accuracy. Various devices, more or less obvious, may be introduced by way of refinement and for the more exact quantification of the incidental errors. The general result of extended observations is to show that the decomposition of the xanthate is in effect continuous, though actual continuity of the analytical numbers are, for the reasons given, not obtainable. It will be evident, however, that we may select some property of the xanthates for observation, involving measurements of 'physical' rather than chemical function; measurements which do not involve a chemical reaction, at least in the sense of a reaction of decomposition. Thus the degree of solubility in 'neutral' dehydrating agents is a property which has been mentioned as varying definitely with the apparent combining weight of the reacting unit. Whereas at one end of the series the xanthates are soluble even in strong alcohol and in salt solutions, they spontaneously pass, in a few hours, into lower terms of the series which are insoluble. For practical experimental purposes, therefore, an observation of the quantity of alcohol necessary to precipitate the xanthate is a measure of its position in the series. But to reduce this to exactitude is not so simple as might at first sight appear, for the reason that the solubility is influenced by the composition and proportion of the incidental by-products. There is the further complication that the alkaline hydrate, necessarily also present, is a specific solvent, whereas the saline by-products, notably carbonate, act rather as precipitants. This matter is still under investigation, and we do not propose to anticipate the publication of the numerical results in their complete form.

It may here be pointed out that the course of decomposition of a given preparation of cellulose xanthate or viscose is

considerably influenced by the conditions which have attended its preparation. Many of these conditions would be easily neglected by operators who are unaware of the individual characteristics of colloids as a class and of cellulose in particular. The following points may all be noted as of importance: (1) The particular cellulose employed; (2) its previous preparation; (3) the concentration and temperature of the alkaline hydrate (solution) employed in preparing the alkali cellulose; (4) the uniformity or otherwise of the alkali-cellulose in respect of the ratio of cellulose to alkali and to water; (5) the period elapsing between the production of the alkali cellulose and its exposure to carbon bisulphide; (6) the initial and maximum temperature of the mass during the reaction; (7) the duration of the exposure to the bisulphide; (8) the mode of treating with water for effecting the solution of the product.

The variations of these factors produces corresponding variations of the final products; thus there are various types of viscose: the normal type, representing complete conversion, producing a homogeneous, structureless solution, which at a concentration of 10 p.ct. (cellulose) will pass through ordinary calico or even paper filters, without residue, other than incidental impurities or foreign matter. At the other extreme, representing imperfect conversion or reaction, the mass will swell, combine, and mix with water to a state rather of indefinite distension, the structure of the original fibres persisting. Preparations of xanthate made on the laboratory scale are usually of intermediate character, approximating to the normal in proportion to the control of the physical conditions. But on the manufacturing scale this control is facilitated by the mechanical aids which are available for milling and mixing of the reagents; and generally the production of 'viscose' of invariable character is assured by regularising the factors above enumerated. In investigating such a problem as that of the spontaneous decomposition of the xanthate in solution, there is an obvious advantage in employing products thus made and from which all minor variations or accidental influences are

eliminated ; and it is from the accumulation of analyses of such products that we are confirmed in the conclusion that the decomposition is continuous. We may cite one or two instances showing the rate of decomposition under ordinary conditions of temperature ; also, by way of illustration, a convenient mode of expressing the change. If we assume a reacting unit (cellulose) of C_6 dimensions, with one OH group giving the typical reaction, the Na combined with the CS.S residue and represented as NaOH will be in the ratio 40 : 162 of cellulose. As decomposition proceeds the cellulose re-aggregates to units of $C_{12} \cdot\cdot C_{48} \cdot\cdot$ dimensions, which is the accepted interpretation of the experimental fact that the 'xanthate Na' expressed as NaOH diminishes in percentage of the cellulose through the series ·· 25 ·· 12·5 ·· 3·125. It is convenient to give the maximum assumed ratio the arbitrary value of 100, and the position of any xanthate in the descending series a corresponding percentage form. The following serial numbers were obtained with particular specimens of viscose, and show the rate of the progressive spontaneous decomposition of the xanthate over periods of 100 hours, at average temperatures of 18 to 22° :

Hours after dissolving	Solutions of xanthate at 10 p.ct. concentration (wood cellulose)					
	A	B	C	D	E	F
5	55	51	—	—	48	—
10	—	—	—	—	—	—
15	45	46	44	—	40	40
20	—	—	—	44	—	—
25	37	40	—	—	33	—
30	—	—	34	—	—	—
35	—	—	—	34	—	31
40	30	36	34	—	28	29
45	—	—	—	34	—	—
50	28	—	32	—	20	—
60	25	—	25	30	14	—
70	—	—	—	—	—	—
80	19	—	25	—	—	—
90	16	—	—	23	—	—
100	—	—	25	23	—	—

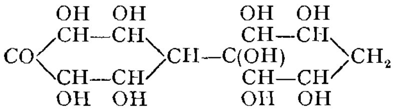
These results show that even with fully converted preparations giving structureless solutions there are considerable variations in the behaviour of different specimens, so far, that is, as the course of change can be measured by an analytical process involving decomposition. It may be noted that the analytical process carried out under the ordinary conditions of laboratory work is, perhaps, not sufficiently regulated, and that for diagnosing the actual condition of a sensitive colloidal compound, which from its very nature is in a condition of progressive change, very minute precautions are necessary for controlling the incidental conditions. The influence of these factors is under investigation. Still more imperative is the necessity of further controlling these methods by independent observations of variations of associated physical properties. *We have always maintained that the study of* these colloidal derivatives cannot be directed otherwise than by attention to the problems raised from within. The particular problem we are now considering is, in simple terms, the question of continuous or interrupted decomposition—in other words, whether there are ascertainable breaks or phases corresponding with particular molecular ratios. But if the question may be formulated in simple terms, the experimental answer is of a highly complex form. As in other cases of cellulose reactions, in proportion to the refinement of method the experimental numbers reveal a closer approximation to continuity. But as regards the colloid these numbers are an indirect, and so far uncertain, measure of its actual condition.

If we approach the solution of these problems on the presumption that no other factors are involved than the stoichiometrical relations and their customary interpretation, we should affirm that the xanthate soda is a direct measure of a specific chemical function of the cellulose, and therefore of its 'molecular weight.' Such interpretation leads to a variable 'molecule' increasing in mass to indefinite dimensions; and this raises the general question as to whether the abstract conceptions associated with the molecular condition of matter are applicable in this and similar cases. Not to reargue this

point on a particular issue, we must limit the discussion to the special aspects of the cycle of reactions involved in the formation and decomposition of the xanthates. In the first place there is no probability of an actual breakdown of the cellulose complex into discrete units of $C_6 \cdot\cdot C_{12}$ dimensions to be again built up by polymerisation into $C_{24} \cdot\cdot C_{48} \cdot\cdot C_{96}$ units; nor is there any evidence that rupture and reaggregation of units of larger dimensions is a necessary interpretation of the combining ratios. We may form an alternative mental picture of a complex of which constitutent OH groups are esterified without in any way resolving the complex, the synthesis being then reversed by dissociation, and the OH groups reappearing in the free or uncombined form. It might be presumed that any constitutional resolution would take the form of hydrolysis, and it has been proved by analyses of the regenerated cellulose that the fixation of water is only fractional in amount—in fact, in the case of wood cellulose the proportion is negligible; cotton cellulose appears to fix water in the proportion $3C_6H_{10}O_5.H_2O$, and the hydrolysis here indicated is only a fractional equivalent of the groups taking part in the cycle of reactions. It is clear, therefore, that the cellulose maintains the general characteristics of an anhydride, so far as can be decided by the initial and final stages of the cycle. We can, for obvious reasons, affirm nothing with regard to the xanthates, as they actually exist in solution. They may represent hydrolysed units, and the process of reversion to cellulose may be accompanied by recombination of the hydrolysed groups. But with a polyhydroxy compound this may occur in a number of ways and as a secondary reaction not affecting the main constitutional type.

Those who would regard cellulose as a polymeride of the type of starch, have perhaps not sufficiently taken into account its inherent resistance to hydrolysis, and the contrast between the two carbohydrates in this respect; or, assuming a phase of hydrolysis, the difficulty of assigning a motive towards reconstituting the anhydride under conditions which influence in the contrary direction, as in the case under consideration.

With the aim of giving a purely 'chemical' interpretation to the reactions of cellulose, and taking particularly into account their many points of contrast with starch, we have in our previous works suggested a poly-cyclo-hexane formula, the essential feature of which is the linking of the unit groups by carbon bonds, thus :



But in view of the exceptionally labile character of the cellulose complex, no final value can be assumed for any constitutional formula ; the only point to be emphasised is that this lability may extend to the central nucleus of carbon atoms as distinct from migrations of oxygen or hydroxyl groups. Actually, however, this view merges into the wider question which arises on the consideration of the typically colloidal characteristics of cellulose. If these are held to be essentially bound up with the constitution, the nature of this relationship becomes a major and previous question. There are particular evidences for the conclusion that molecular constitutional formulæ cannot represent the condition of the constituent groups of cellulose as it exists in the aqueous solution of derivative compounds. These 'solutions of cellulose' have been previously represented, in accordance with 'molecular' views, as colloidal 'double salts' resulting from reciprocal interaction of acid and basic groups of the 'saline solvent' and of the cellulose. Much has been added by the investigations recorded in the present volume to our knowledge of cellulose as typically amphoteric and especially labile in its relation to acid and basic reagents. But we have to apply to these complex compounds the general knowledge we have of solutions, and the particular deductions which are now in active circulation concerning the colloids as a class. We are thus led to a mental picture of the condition of the constituent groups of cellulose in solution, similar to that which we should form of the solution of a salt of polyvalent radicles, feebly basic and

acidic. This imports the conceptions of ionisation of reactive constituent groups, which are not the assumed molecules but sub-groups or residues resulting from resolution according to electrolytic actions. From this point of view the state of matter in a 'solution of cellulose' must necessarily be extremely complex. With dissociation there are the complementary features of association and aggregation, and the functions of water in both groups of phenomena. If these relations are still the subject of active controversy, even where the simplest electrolytes are concerned, we cannot expect to formulate in any detail and for general acceptance a comprehensive account of the phenomena attending the solution of cellulose. We would make one general statement which may enable us to more clearly define the issue.

The crystalline salts may be defined as *extrinsic electrolytes*—that is, to become conductors of the current they require to change their state, by fusion or solution; the colloidal salts and amphoteric compounds of the order of cellulose we regard as *intrinsic electrolytes.* In the separation of a crystalloid from solution the phase of dissociation or ionisation is reversed, the molecular equilibrium is restored, and the crystalline form reappears. In the solution of a colloid, in water, for instance, the colloid itself undergoes no essential change; it is diluted or distended, is homogeneously distributed through the solvent, though perhaps the terms solvent and solute may in such cases be regarded as interchangeable. In the reversal of the process and the separation of the colloid, the solid phase is continuous with the fluid phase: the solid colloid may be said to exist preformed in the solution. The colloid does not consist of electrically neutral molecules, as does the solid crystalline 'electrolyte,' but is formed under the condition of electrolytic stress, which stress is retained and expressed in the configuration of the constituent groups. This shows itself under the influence of hydrolytic agents—that is, of H or OH ions—for changes of configuration immediately occur and increase with the duration and intensity of the reaction.

We have introduced this general statement in order to

point out the application of the deductions to the particular case of the cycle of reactions which are under consideration.

1. *The Alkali-cellulose Reaction* presents certain features not brought to light by the investigation of its external aspects, generally summed up in the term 'mercerisation.' Thus it is stated by all investigators of the technical process of 'mercerisation' that the time-factor is of purely subordinate moment ('Die Mercerisation der Baumwolle,' P. Gardner, pp. 112–114). But as a matter of fact the immediate reaction, with its accompanying structural changes, is succeeded by changes which profoundly modify the xanthate reactions and the properties of the xanthate solution (viscose) obtained. Thus, by merely varying the time-factor, it is possible to obtain viscoses of equal viscosities containing any proportion from 3 to 15 p.ct. of cellulose in solution. So also the progressive advance to a structureless viscose is in direct relation to this time-factor, and the interior changes continue after this phase has been reached, and are then measured by the physical properties (viscosity) and relative stability of the solution.

What is the nature of these changes? In the first place, there is an acidification of the cellulose. The cellulose not only shows a superior acid function in its reactions with bases in presence of water, but manifests an extraordinary resistance to esterification. Thus to the acetylating mixture, which depends upon the catalytic action of sulphuric acid (Lederer), the cellulose regenerated from viscose shows itself indifferent, whereas the original cellulose is rapidly dissolved (as acetate). Even the action of nitric acid may be so regulated as to leave the former cellulose almost unattacked, under conditions which convert the latter into a high nitrate.

In the second place, it is to be noted that this change of chemical function is not attended by change of weight of any moment; it is not a consequence of the fixation or withdrawal of groups reacting with the alkaline hydrate. It is evident that there is a change of configuration both of the complex and the component unit groups, but the nature of this change must remain for the present a matter of conjecture. It may

be pointed out that the acidification of the cellulose is produced by mercerisation under the usual conditions of short exposure to the action of the alkaline hydrate. The progressive further modification which follows is only brought into evidence by the xanthate reaction—that is, by the diminishing viscosity of the solutions of the xanthates produced and their increased stability. This suggests a progressive resolution of complex aggregates into simpler component groups; but we cannot affirm anything as to the nature of this resolution. We might conceive the action rather as a progressive polarisation in which the electro-positive and electro-negative groups take up definitely related positions—the effects of which would be similar to an actual break-up of complexes, such as are held to characterise the hydrolytic resolution of starch. These considerations reappear in an analysis of

2. *The Reaction of the Alkali-cellulose with Carbon Bisulphide.*—It would appear, for obvious reasons, that the reaction takes place with the electro-positive hydroxyls, with the result of a still further net gain of electro-negative potential and, as a final result, a completely water-soluble saline product. Are we to assume that at any stage there is an actual rupture of these unit antipodes as a result of their varying potentials, or may we assume that they co-exist in polar complexes? Seeing that throughout the whole cycle of reactions of synthesis and reversion the cellulose undergoes no mass or weight changes of any moment; that all these reactions and changes take place within a circumscribed field—that is, the unit mass of cellulose; that what we have under observation in all our experimental inquiries is to all intents and purposes this unit mass; that we can only hope to penetrate the present mystery of this complex mass by the application of physical methods, and that up to the present no such method giving direct measurements is available—we may be excused from attempting a final answer to any of these questions. We have raised them for the purpose of exhibiting the complexity of the problems involved, at the same time setting out the lines upon which investigation must proceed.

9 (*a*).

INFLUENCE OF CERTAIN REAGENTS ON THE TENSILE STRENGTH AND ON THE DYEING PROPERTIES OF COTTON YARN.

J. HÜBNER and W. J. POPE (J. Soc. Chem. Ind. 1903).

A necessary basis of this investigation was a preliminary critical inquiry into generally accepted methods of experimentally determining breaking-strains, and of reducing the results to a 'mean tensile strength' with a quantified mean error. The authors finally adopted the method of breaking single threads in a 'Schopper' machine (Mitt. K. K. Versuchsanstalt 1901), taking a large number of observations and quantifying the probable mean error of the mean value. The latter is then reduced to ±0.7 p.ct. as a maximum.

The material to serve as the basis of observation was an Egyptian yarn prepared by boiling with water and subsequently with a solution of soda (1 p.ct. Na_2CO_3), finally purified by exhaustive washing and air-dried.

The comparison of the yarn thus purified with the original raw yarn is given in the following numbers:

Breaking strain in grms.	original	370 ± 1·7
	treated	417 ± 2·1

We now quote the authors in extenso:

'It appears therefore that during the boiling and steeping in water, and the boiling in a 1 p.ct. sodium carbonate solution, the tensile strength of a raw cotton yarn increases considerably. This increase in strength would seem to be attributable to the boiling in water, and not to the action of the sodium carbonate, which only serves the purpose of removing greasy matters; this is indicated by a third set of determinations made upon a lea of the material A after it had been scalded,

left for six days in a 15 p.ct. sodium carbonate solution, and washed and dried.

'This gave a mean tensile strength, 419·7 ± 2·2 grms., which is numerically identical with that for the purified yarn, 417·4 ± 2·1 grms., and it therefore seems that a 15 p.ct. solution of sodium carbonate has no more action on the tensile strength of the yarn than a 1 p.ct. solution.

'No satisfactory explanation, based on experimentally determined facts, has yet been offered for the considerable changes in the tensile strength of cotton yarn which result from chemical treatment of the yarn; further, no quantitative explanation of the variation in tensile strength of different threads from the same lea of yarn has yet been given. Now, however, that we have determinations of the tensile strength of yarn possessing a known and high degree of accuracy, we are able to put forward tentatively conclusions concerning the points mentioned, reserving for a later date a more complete experimental study of the conditions than is possible in this preliminary paper. A little consideration will show that the tensile strength of a yarn which contains n fibres in the cross-section is but remotely connected with the tensile strength of the n individual fibres, for, on breaking a thread by the application of a certain load, the mean effect of the load is to pull the fibres apart, a much smaller number than n being broken, and being broken at different times. So long as the tensile strength of the yarn is less than n times the tensile strength of a single fibre, the strength of the fibres is of quite subordinate importance, and the main factor determining the strength of the yarn is the closeness of the twist, and, perhaps also, a specific adhesion or "cling" exerted between the fibres; it would be expected, therefore, that variations in the twist would show themselves in variations in the tensile strength of the yarn. Mr. W. Myers kindly made a series of 58 determinations of

the twist on 10-in. lengths of the raw Egyptian yarn used in the present work, from which it appears that the twist varies from 22·0 to 30·3 turns per in., the mean being 25·66 turns per in. The twist being the main factor in determining the tensile strength of a cotton yarn, it is interesting to notice that the above three figures relating to the twist of the yarn, viz. 22·0, 30·3, and 25·66, are in the ratio 324 : 446 : 378, which is practically the same as the ratio 330 : 440 : 378, of the lowest, highest, and mean values of the tensile strength determined. This would indicate that for one and the same yarn the tensile strength is directly proportional to the twist.

'On making a count of the fibres in the yarn with which we have worked, it was found to contain an average of 100 fibres in the cross-section. If the above reasoning is correct, each fibre of the raw yarn has a tensile strength greater than 387/100, or 3·87 grms.; and further, if a series of tests be made under conditions which interpose a resistance to the drawing apart of the fibres, and which increase the number of fibres which have to be broken before the yarn breaks, a great increase in the tensile strength of the yarn should be observed. These conditions would be attained by making the length of thread to be broken less than the average staple of the yarn. We give determinations of the tensile strength of the raw yarn made by diminishing the distance between the clips in the tearing machine to 1 mm., so that the yarn is broken in lengths of 1 mm. instead of 100 mm. as in the trials given previously for the raw yarn.

'The tensile strength thus determined on a length of 1 mm. is 479·4 ± 3·4 grms., whilst that made on a length of 100 mm. is 378·0 ± 1·7 grms., so that, as was to be anticipated, the very short length gives a very much higher tensile strength. Determinations of the tensile strength of single fibres, as also

an investigation of the relation between the length of thread broken and the mean tensile strength, are now in progress.'

The authors extended their observations to a number of solutions producing effects of 'mercerisation' more or less pronounced. The results are summarised in the form of tables, which we reproduce, together with the general discussion of the results which follow :

'The quantitative results given in the previous pages may be conveniently summarised as in Table A, in which the table from which the results are taken is given in the first, and the tensile strength, *t*, in the third column. The tensile strength, reduced to that of the standard material, as a basis of 100, is stated in column 4, and the limits of measurement of *t* and the ratio of those limits, are stated in columns 5 and 6.

'It is interesting to note that the widening of the limits of the observed tensile strengths is accompanied by a comparatively slight increase in the probable mean squared error of the mean, and that in spite of the wide limits between which the observed tensile strengths lie in many cases, the probable error is never more than 0·7 p.ct. It is further important to notice that when the mean tensile strength is greatly increased by the application of any chemical treatment which we have studied, considerable disturbances in the structure of the yarn take place, as is indicated by the great widening of the limits of the observed tensile strength in such cases.

'In the previous pages we have not yet discussed the shrinkage which results from the subjection of the standard yarn to treatment; the length of the leas of yarn before and after treatment were ascertained by hanging the lea on a hook, suspending a weight of 25 grms. from it, and measuring the length of the lea as accurately as possible with a millimetre scale. The lengths (*l*) in centimetres are given in column 4 of Table B. During the determinations of the tensile

strength of the various treated yarns, observations were made of the elongation at the breaking load of each thread; these elongations vary very considerably amongst threads from the same hank, and for our present purpose it suffices to state the mean percentage elongation of the yarn at the breaking load. These numbers are stated in column 5 of Table B, and from the lengths of the hanks and the elongations we have calculated the mean lengths (l_1) to which the hanks will stretch on application of the breaking load; a comparison of the values of l and l_1 shows clearly that after a yarn has been shrunk by mercerisation or other treatment and washed and dried, it cannot be stretched to its original length without breaking.

'Thus 66·0 cm. of raw yarn is shrunk to 45·2 cm. by mercerising without tension, washing and drying, and on afterwards stretching the mercerised thread to the breaking-point it only attains a length of 58·0 cm.; this is a result of peculiar interest in view of the fact that the 66·0 cm. thread of raw yarn could be mercerised and washed under tension, and caused to retain that length after drying as mercerised cotton.

'We have indicated above the great probability that the twist is the controlling factor in determining the strength of a yarn, and have given evidence suggesting that for one and the same sample of yarn the tensile strength is directly proportional to the twist. The twist in the samples of yarn produced by the various kinds of treatment mentioned is naturally inversely proportional to the length l of the lea, so that if the law just suggested is also applicable to a yarn, independently of the chemical treatment which has been applied, the product of t and l should be constant throughout the series of trials now discussed; the values of $t \times l$ are given in column 7 of table B and in column 8 are stated the values of $t \times l$ reduced to the $t \times l$ value of the material A

TABLE A.

—	Treatment of yarn	Tensile strength t	t reduced to III. as 100	Limits of observed tensile strength	Ratio of limits. 100 to—
II.	Raw yarn	378·0 ± 1·7	90·6 ± 0·40	330 and 440	133·3
III.	1 p.ct. Na_2CO_3 solution	417·4 ± 2·1	100·0 ± 0·50	285 „ 510	179·0
IV.	15 „ „ „	419·7 ± 2·2	100·6 ± 0·53	325 „ 505	155·4
V.	NaHO solution, 1 day	530·9 ± 3·8	127·2 ± 0·90	355 „ 665	187·3
VI.	„ „ 6 days	526·3 ± 3·8	126·1 ± 0·90	400 „ 675	168·7
VII.	„ „ „	523·9 ± 3·5	125·5 ± 0·84	355 „ 700	197·2
VIII.	Raw yarn, 1 mm.	479·4 ± 3·4	114·9 ± 0·81	360 „ 590	163·8
IX.	KI solution, 1 day	431·6 ± 2·3	103·4 ± 0·56	305 „ 520	170·5
X.	„ „ 6 days	420·4 ± 2·1	100·7 ± 0·50	315 „ 500	158·7
XI.	BaI_2 solution, 1 day	433·4 ± 3·0	103·8 ± 0·72	310 „ 570	183·9
XII.	KI, HgI_2 solution, 1 day	444·9 ± 2·9	106·6 ± 0·71	330 „ 590	178·7
XIII.	„ „ 6 days	443·3 ± 2·7	106·2 ± 0·65	325 „ 575	176·9
XIV.	BaI_2, HgI_2 solution, 1 day	534·3 ± 3·9	128·0 ± 0·92	395 „ 670	169·6
XV.	„ „ 6 days	526·6 ± 3·3	126·1 ± 0·79	425 „ 715	168·2
XVI.	VII. with KI solution	503·0 ± 3·3	120·5 ± 0·80	370 „ 625	168·9
XVII.	VII. boiled with water	505·0 ± 3·5	121·0 ± 0·84	370 „ 650	175·7

TABLE B.

—	Treatment of yarn	Mean tensile strength = t	Length in cms. = l	Elongation at breaking load	Length at breaking point = l_1	$t \times l$	$t \times l$ to III. as 100	$t \times l_1$	$t \times l_1$ to III. as 100
				p.ct.					
III.	1 p.ct. Na_2CO_3	417·4	66·0	9·29	72·1	2755	100·0	3011	100·0
IV.	15 „ „	419·7	65·6	9·56	71·9	2753	99·9	3016	100·2
V.	NaHO, 1 day	530·9	45·2	28·24	58·0	2400	86·9	3077	102·2
VI.	„ 6 days	526·3	44·8	27·12	57·0	2358	85·6	2997	99·6
IX.	KI, 1 day	431·6	65·0	9·83	71·4	2805	101·8	3081	102·3
X.	„ 6 days	420·4	64·6	9·86	71·0	2716	98·6	2984	99·1
XII.	KI, HgI_2, 1 day	444·9	65·2	10·00	71·7	2901	105·3	3191	106·0
XIII.	„ 6 days	443·3	57·3	16·35	66·7	2540	92·2	2955	98·2
XIV.	BaI_2, HgI_2, 1 day	534·3	52·3	20·52	63·0	2794	101·4	3368	111·9
XV.	„ 6 days	526·6	48·9	24·62	60·9	2575	93·5	3209	106·6

(from III.) as a basis of 100. The values in these two columns show a considerable tendency towards constancy.

'But it is not quite legitimate to expect constancy in the values of $t \times l$, because at the breaking-point the load t is not being applied to the length l but to the length l_1; and the product $t \times l_1$ would be more likely to be the constant quantity. This value is given in column 9, and in column 10 is reduced to the $t \times l_1$ value of the standard yarn as 100; with the exceptions of the hanks treated with potassium or barium mercuric iodides, all the $t \times l_1$ values lie between 99·1 and 102·3—that is to say, they are identical within the limits of the experimental error incurred.

'It may thus be safely concluded that although during mercerisation a yarn shrinks by about one-third, its tensile strength remains directly proportional to the twist.

'It should be noted that if, on chemical treatment, the cotton fibre preserves an unaltered volume but merely changes in length, the length l is inversely proportional to the cross-sectional area a of the fibre, so that $l \times a$ is equal to the constant volume. But if a given volume of material be made up into rods of different lengths and uniform thicknesses, the breaking loads of the rods will be directly proportional to the cross-sectional area and inversely proportional to the length. This result is of the same form as that obtained in the present investigation.

'The value of a yarn for manufacturing purposes must be to a considerable extent dependent upon the uniformity of its twist—that is to say, a yarn which will withstand the various operations of bleaching, mercerisation, dyeing, weaving, &c., without giving great trouble owing to frequent breakages, must be one in which the limits of the observed tensile strengths measured on about a hundred separate threads do not lie too far apart. The limits of the observed tensile strength for the

leas of differently treated yarn which we have examined are given in Table A, and are conveniently discussed after reducing them to the basis of the lowest observed breaking load as 100; the quantities thus deduced, which may be termed the 'ratios of the tensile strength limits,' are also given in the table, and will be seen to vary widely for leas which have been subjected to different treatment. Yarn No. II., in which the ratio of the limits is as 100 to 133·3, must obviously give far less trouble during weaving owing to broken threads than that numbered III., in which the ratio is as 100 to 179·0. It seems, therefore, that the manufacturer would derive very reliable information as to the behaviour of a yarn during the subsequent manufacturing processes from the determination of this ratio of the limits of the observed tensile strengths, or by the comparison of the mean tensile strength with the tensile strength observations lying below the mean value. The data obtained in the way which we now describe, treated by the method which we have used, affords specific information as to the strength and the variation in strength of a yarn, whilst the figures given by the lea testing-machine ordinarily used are meaningless in so far as the tensile strength of the yarn is concerned.'

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9 (*b*).

THE LUSTRE, THE TINCTORIAL PROPERTIES, AND THE STRUCTURAL ALTERATIONS WHICH RESULT FROM TREATING COTTON WITH MERCERISING AND WITH OTHER LIQUIDS.

J. Hübner and W. J. Pope (J. Soc. Chem. Ind. 1904, 23).

This communication aims more directly to elucidate the technology of the mercerising process, but necessarily contributes to a knowledge of the primary factors involved in the

interaction of cellulose with the alkaline hydrates in presence of water. The main points considered are the specific changes in the properties of the cellulose, resulting from treatment with a series of caustic soda solutions of progressively increasing concentration in NaOH—viz. (1) in affinity for direct-dyeing colouring matters; (2) in dimensions, as measured by shrinkage of a standard cotton yarn; and (3) in associated structural details.

The increase of avidity under (1) was measured by quantitative dyeings with benzo-purpurin 4 B, using 0·25 p.ct. of the weight of the cellulose. The progressive increase is graphically represented by a curve, generally regular in character, but marked by certain phases of more rapid increase. The experimental observations may be briefly summarised as follows:

1. Solution at 0° to 18° Tw. Effect approximately proportional to concentration in NaOH.

2. At 18° to 22°. A more rapid proportional increase of dyeing capacity.

3. At from 22° to 26°, and again from 26° to 30°. Two further stages of increased disproportion.

4. At 30° to 40°. A diminishing effect approximately one-fifth of that in the preceding stages (3), still further diminishing at and above 45°.

5. At 55° to 70°. The maximum effect, with very slight variation for varying concentration.

6. At 70° to 80°. There is a reversal of the effect, and cotton treated with the solution at 80° (1·4 sp.gr.) is at about the same level of dyeing capacity as the same cotton treated at 35° (1·17 sp.gr.).

(2) The associated structural changes are most obviously demonstrated by shrinkage in length of a standard cotton yarn; a special method was devised to bring the measure-

ments to a degree of exactitude consistent with the observation of the differences due to increments of 0·005 in the specific gravities of the solutions of NaOH.

The results of observations are given in the subjoined table, which records the reduced lengths of skeins of 200 yards initial length, after treatment for 30 minutes in the cold and measured whilst still moistened with the solution:

Strength of soda. ° Tw.	Length of hank after treatment	Strength of soda. ° Tw.	Length of hank after treatment
0	198·0	22	171·3
1	196·4	24	163·1
2	195·7	26	160·3
3	195·6	28	160·0
4	195·5	30	158·2
5	195·2	35	150·2
6	194·2	40	143·7
7	193·7	45	141·0
8	194·2	50	142·2
9	194·0	55	142·7
10	194·2	60	145·3
12	194·5	65	149·2
14	192·7	70	150·3
16	190·4	75	152·8
18	188·7	80	154·2
20	186·8		

The progressive effects may be summarised as follows: A shrinking effect (>1 p.ct.) is observed with the weakest soda compared with the action of pure water. From 1° to 20° the shrinkage shows a fairly uniform increase; at 20 to 22° there is a sudden increase, and again at 22° to 24°; the increase of shrinkage continues at a relatively rapid rate until the maximum is reached at 45°. Above this point of concentration of the NaOH the contraction of the yarn continuously diminishes. The results, plotted as a curve, are seen to be generally coincident with the corresponding variations of dyeing capacity.

(3) The changes in minute structure have been very closely

investigated by the authors, and while they confirm the general effects described by previous observers (see 'Researches on Cellulose,' p. 24), they have brought out an additional and special structural feature of the mercerised fibres—viz. the development of spiral but rounded enlargements of the surface, which in their opinion are the particular cause of the silky lustre of mercerised cottons. The microscopic observations were also extended to the actual process. The action of solutions of varying concentration upon loose cotton-fibres placed under observation in a microscopic field are carefully described. The two main effects observed are the swelling of the fibre-substance and the uncoiling of the fibres, and the authors conclude that for the production of lustre the latter effect must not precede the former. This conclusion was confirmed by observation of structural changes caused by various reagents in more or less concentrated solution, such as zinc chloride, phosphoric acid, nitric acid (1·41 sp.gr.), sulphuric acid, sodium sulphide, barium, mercuric iodide (saturated solution). The gradation of shrinking and swelling actions of these solutions were examined in reference to gradations of lustre of the treated cottons. Generally, the inferior actions of these reagents, by comparison with those of sodium hydrate, are traceable either to relatively feeble swelling or uncoiling action, or to the fact that untwisting of the fibre precedes the swelling action.

10.

CELLULOSE AND COLOURING MATTER; THEORY OF DYEING.

It is in accordance with the development of our subject to regard a dyed cellulose as a synthetical compound of cellulose and colouring matter. Even if we give full value to the con-

tention of controversialists who aim at establishing a mechanical or physical 'theory of dyeing,' as against a chemical interpretation of the phenomena, it is obvious that the evidence which leads us to regard the hygrometric equilibrium of cellulose as an essentially chemical phenomenon applies *à fortiori* to dyeing processes. The combination of cellulose with 'hygroscopic moisture' is reversible under small variations of temperature: it is in every sense a variable equilibrium. The affinities in play are certainly feebler than in a large number of cases of dyed celluloses, and 'the absence of any definite limit' is sufficient, according to Masson (*loc. cit.*), to dispose of the view of the combination resulting from 'chemical affinity.' While therefore fully admitting the facts which are objected to a chemical interpretation of these residual affinities, we have to ask whether the objectors would maintain their contentions in view of the converging proofs which are accumulating in the investigations of cellulose now under review?

It appears to us that the phenomena which it is attempted to exclusively group under a 'theory of dyeing' are far too complex and heterogeneous for a satisfactory generalisation. But what is more evident is that this has been attempted before we have come to any agreement as to the fundamental chemistry of the fibre colloids. In the various recent publications on this subject all the conditions of the phonomena are investigated, more or less exhaustively, save and except the all-important factor, the reactivity of the fibre colloid considered generally in relation to the colloids as a class, and, or more particularly, in reference to their many distinguishing characteristics. We were impressed with this want of proportion at the time that we wrote upon the subject in 1886, in a series of articles in a technical publication—'The Dyer'—and it may be of interest to reproduce the substance of that communication.

In a preface, the inadequacy of classification of phenomena of this order under the apparent antithesis 'chemical' or 'physical' is set forth, with illustrations drawn from the wide

range of hydration effects. The following passage then occurs: 'The study of this one subject of hydration, or water combination, together with the thermal phenomena by which it is attended, leaves us impressed with our inability to draw any line between the several types of combination. . .

'It is scarcely necessary to point out that the dyeing of fabrics or tissues is only a particular case of the absorption of substances from solution, or, still more generally, of transference by molecular action from one liquid medium to another.

'The simplest case of such a transference is afforded by the removal of a substance dissolved in a liquid by one having a "stronger attraction," into which the substance therefore passes when the two liquids, mutually insoluble, are brought into contact.

'Take the case of the aqueous solution of iodine. This solution, when shaken with carbon disulphide, is deprived of its iodine, which passes over into the latter menstruum, forming a purple solution; the aqueous solution, on the other hand, being yellow. Should we class these phenomena as physical or chemical?'

The point thus illustrated by the solution equilibrium of iodine as between water and carbon bisulphide is then further discussed.

The particular reactions involved in the mordanting and colouring of the 'organic' fibrous colloids by compounds of colloidal characteristics, with water as the intervening and conditioning agent, can only be investigated on the basis of an understanding of the colloidal state. A general account is therefore given, first of the researches of Graham, and especially of his conclusions as to the continuity of the colloidal state through the soluble and insoluble forms; secondly, of the researches of van Bemmelen on the withdrawal of acids, bases, and salts from solution by colloidal hydrated oxides (J. Prakt. Chem. 2, 23, 324), with special reference to the quantitative relation of these absorptions to the degree of hydration of the oxides; thirdly, of the researches of Mills and Takamine on the

absorption of acids and bases from solution by the 'organic' fibre colloids ('J. Chem. Soc. 1883, 153), all of which manifest the amphoteric character.

In commenting on these results the following passage occurs : 'The authors make no allusion to the change wrought upon the fibres under the action of these reagents, but these, we think, should not be overlooked. We are familiar with the lustre and touch of "scrooped" silk, as compared with the "deadness" in appearance and feel of silk dried from an alkaline solution; and the effects of acids and alkaline solutions upon cotton, though not so marked, are considerable and of the same order.

'We are not so much concerned with the definition of these changes as "mechanical" or "chemical." Even if slight they are proportionate to the "absorptions" we have been dealing with, and, extending the author's conclusions, we may class them as chemical. The main conclusion to be drawn is that these fibres or fibre-substances have a certain molecular activity, which manifests itself when they are brought into contact with hydrolytic reagents of the two orders, acid and alkaline.'

It is pointed out that these fibrous colloids are capable of an extended series of hydrolyses and that these decompositions are probably preceded by union with the hydrolytic agent, as in the case of the saponification of the fatty ethers, where the emulsion stage probably represents the combination of the complex ester with the alkaline agent, in its hydrated form, preceding the actual resolution into glycerine and fatty acids.

In conclusion, it is pointed out that the cellulose group supplies a wide range of variations of structural and chemical type, both (1) of 'natural' origin, and (2) of laboratory production, the latter including synthetical derivation, and products of resolution by the action of hydrolytic and oxidising agents. Many instances are already known, in which dyeing capacity varies directly with variations in chemical constitution and independently of structure; and a 'theory of dyeing' is

premature until these complementary phenomena have been more exhaustively studied.

We wrote this some twenty years ago and merely reproduce it as a document which, in reference to the controversy still being waged, is an evidence of the slow progress made towards an agreement.

We proceed to notice certain more recent contributions to the subject, though not at length, for the reason that the matter must be subordinated to the general perspective of the subject.

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10 (*a*).

INORGANIC COLLOIDS AND TEXTILE FIBRES: A CONTRIBUTION TO THE THEORY OF DYEING.

W. BILTZ (Nachr. Wiss., Göttingen, 1904, 1).

Ueber das Verhalten einiger anorganischen Colloide zur Faser in seinen Beziehungen zur Theorie des Faerbevorganges.

The author has investigated the behaviour of cotton and silk towards colloidal solutions of a widely varied range of inorganic substances, including elements—selenium, tellurium, gold; oxides—vanadium (pentoxide), molybdenum ('blue'), tungsten (blue); and sulphides—cadmium, arsenic, and antimony sulphide. These compounds are taken up in varying proportions by the fibre-substances, and their 'adsorption' was found to have no relation to chemical constitution or function. The dyeing process would appear therefore to be a purely physical effect; and if the analogy of these inorganic types with the substantive dyestuffs may be assumed, it may be concluded the dyeing properties of these latter are not essentially related to their saline constitution. But an experimental inquiry carried out by the Akt. Ges. für Anilinfabrikation, Berlin, showed that the inorganic colloids cannot be compared with the substantive dyes in proportionate dyeing effect, neither in

the quantity 'adsorbed' nor in the resistance of the dyed fibres to washing and to rubbing. It is noted that dyeings with the inorganic colloids can be made much 'faster' when produced by double decomposition within the fibres.

The author draws no conclusion from these observations and leaves the general question entirely open on the alternative issues—i.e. whether colloidal characteristics or saline constitution are the dominant causes of dyeing effects.

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10 (*b*).

COAL-TAR COLOURS IN RELATION TO STARCH, SILICA, AND SILICATES.

W. SUIDA (Sitzungsber. Wien, July 1904).

Ueber das Verhalten von Teerfarbstoffen gegenueber Staerke, Kieselsaeure, und Silikaten.

Starch.—A series of dyeings with cold solutions of typical dyestuffs established the following general results: The basic dyestuffs give water-fast colorations; dyeing power diminishes with the introduction of sulphonic groups. The dyeing effect appears to be referable to a combination of the dye-base with the starch complex; the acid component is saturated by basic constituents of the ash of the starch, and is left in the dye-bath in the form of neutral salt. The starch behaves similarly to the animal fibres, and to hydro- and oxycellulose, but is differentiated from cellulose. Similarly, but conversely, whereas cellulose is dyed directly by the majority of diamine colours, starch is not. The only exception so far disclosed is in the case of the azo-derivatives of diamido-stilbene.

Miscellaneous Inorganic Substances, including sulphur, calcium, and other sulphates, magnesium and other carbonates,

aluminium oxide and phosphate, zinc oxide, china clay, talc, kieselguhr, pumice, were treated with solutions of basic dyestuffs, both hot and cold. The silicates alone were dyed. To a typical selection of acid dyestuffs these silicates were inert.

Silica and Silicates.—An extended series of experiments are recorded with a careful selection of silicates of known composition.

The general result with the basic dyestuffs was the absorption and retention of the base by the acid groups of the mineral, the acid components of the dyestuff being saturated by the basic constituents of the mineral. The dyeings were carried out quantitatively upon a selected china clay, and the proportions of the colour bases fixed were found to be constant. The author concludes finally that 'adsorption' effects play only a subordinate part, and the major effect is a saline combination of dye-base and silica, modified only by the condition of hydration of the mineral.

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10 (*c*).

THE DYEING PROCESS IN RELATION TO ACTIVE MOLECULAR GROUPS OF FIBRE-SUBSTANCES.

W. Suida (Sitzungsber. Wien, January 1905.)

Ueber den Einfluss der activen Atomgruppen in den Textilfasern auf das Zustandekommen von Faerbungen.

The author made some confessedly unsatisfactory attempts to prepare definite esters of cellulose, and obtained a monobenzoate and a mono-acetate (C_6) by the action of the anhydrochlorides in presence of bases; but the cellulose was simultaneously converted into hydrocellulose. These products, together with a cellulose nitrate (12·1 p.ct. N), were dyed comparatively with a normal cotton in baths of basic, 'direct,'

and azo-acid dyestuffs. No differences were observed in the comparative behaviour of the cellulose and its derivatives.

The conclusion drawn is that the OH groups of cellulose are of feeble activity, and that the dyeing of cellulose must be referred to such physical agencies as dissociation, adsorption, capillarity, and solution effects. Silk and wool were treated with acetyl and benzoyl chlorides on the one hand, with alcohols and sulphuric acid and alkyl bromides on the other. The new derivatives were compared with the original fibres for dyeing capacity. The general effect of bringing the acid groups of the animal fibre-substances into previous synthetical reaction, was to suppress their avidity for basic dyes.

The dyeing capacity of these products is clearly bound up with 'saline' constitution and reciprocal interaction with the acid and basic components of colouring matters.

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10 (*d*).

THEORY OF DYEING, PART II.; PSEUDO- AND DE-SOLUTION.

W. P. DREAPER (J. Soc. Chem. Ind. 1905).

This is a continuation of the essay previously appearing in the same journal (1894, pp. 95–101). It is in the main a critical study of recent literature on the subject of pseudo-solution, 'surface concentration,' capillary actions, osmotic phenomena, association and dissociation, generally of the 'physical' conditions which necessarily accompany dyeing reactions, and which on the author's *résumé* are the effective causes, rather than synthetic reactions, in the chemical sense, between the active component groups of fibre-colloids and colouring matters.

The final conclusions may be given in the author's own words:

'The conditions of dyeing would seem to be as follows:

'1. A solution of dye or mordant within certain (i.e. definite) limits of aggregation.

'2. State of fibre corresponding to this degree of aggregation.

'3. Effective "localisation" of the dye, with subsequent concentration of the dye in the fibre-substances.

'4. De-solution, due to secondary attraction between fibre-substance and dye, or concentration effect.

'5. In rare cases primary or chemical attraction may play some part in the process at this stage.

'There is no evidence in favour of solid solution in any of the above results, even in its recent and wider aspect. As is seen dyeing may take place on purely physical lines and, anyway, any chemical action would seem to be of a secondary nature and not essential to the process.'

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We have noticed these recent contributions to the subject since they are typical of its literature; they indicate the present position of the controversy and the conflict of conclusions which prevail. As a general criticism, we may remark that these contributions do not consider, and still less attempt, to exhaust cases which are recognised to be typical, perhaps exceptional. Thus, A. G. Green's primuline dyed upon cotton is a case of special 'affinity'; its union with the cellulose is not affected by conversion into the diazo-compound, and this derivative shows a sensitiveness to light very considerably greater than that of the diazo-primuline in the free state. We take this as an evidence of molecular simplicity, of dissociation rather than aggregation.

Further, there is no assignable limit to the dilution of a primuline dye-bath which would inhibit its removal by

cellulose in a condition of uniform distribution. In this instance, both as regards the mechanism of the dyeing process and the condition of the colouring matter within the fibre colloid, we recognise a complete inversion of the perspective of principles formulated by Dreaper.

The contrast of the dyeing properties of jute and flax enable us to reduce the question of minute structural characters to its true dimensions in relation to operative causes. These fibres are morphologically very similar; outside the disparity in length and the complexity of the fibre-bundles in jute, there are no marked features of differentiation. Jute, however, has a many-sided avidity for colouring matters. Flax and flax cellulose, on the other hand, are feeble and selective in their dyeing capacities. There is no need to elaborate the purely chemical causes of these divergent relationships.

A further contribution to this aspect of the probable causes is the contrast in the dyeing capacities of the 'artificial silks' and the normal celluloses. If capillary and minute structure played any essential rôle in true dyeing phenomena, the disparity would be in favour of the 'natural' fibres. But it is in favour of the structureless forms of cellulose (hydrates), and is obviously influenced by two causes which are strictly 'chemical'—i.e. the hydration changes which accompany this chemical treatment of synthesis and decomposition, and the change of configuration of the aggregate giving the OH groups a more acid character than the original.

As a special type illustrating both the mechanism of the process and the ionising activity of the fibre colloid, we may again cite the interaction of the ligno-celluloses with ferric-ferricyanide. We have seen no reason to change our views as to the essentials of this reaction—i.e. (1) that the ferric-ferricyanide is absorbed as such, as a result of colloidal isomorphism; (2) the complex is dissociated by the fibre colloid, owing to the avidity of its 'unsaturated' quinonoid component for oxygen. Prussian blues are formed in a condition of maximum hydration, and consequently uniformly distributed in solid solution in the fibre-substances.

Our contention is that the investigation of these and many other cases of this order, upon which there would be, or might be, a preliminary understanding amongst the controversialists as to typical characteristics, would carry us much further than experimental inquiry over a wide range of colouring matters with relatively little attention paid to the special chemistry of the fibre-substance or of the colloidal state.

Thus we think the lines of investigation pursued by Pope and Hübner (*loc. cit.*), whose contribution requires to be again mentioned in connection with this section of our subject, is much more promising of illustrative results than a diversified research in which no definite account can be given of the variations of the dyed material considered as a chemical individual.

It will be evident also, as is in fact generally recognised in all recent contributions to the subject, that the phenomena of dyeing involve as a fundamental factor the rapidly evolving theory of the colloidal state. The most promising phase in this evolution is, in our view, that which we owe to the initiation of E. Jordis, who in the brochure previously mentioned (p. 6), entitled 'Neue Gesichtspunkte zur Theorie der Kolloide,' generalises the critical phenomena presented by the colloids as consequences of the modern 'theory of solutions.' A study of this brochure leaves the reader impressed with the fact that the author's exposition implicitly involves the phenomena of the dye-bath at every point. As particularly referring to the special points above considered, we reproduce one or two passages: 'Hydrosols are formed and maintained by chemical causes only. In the transitions to hydrogels chemical reactions are mainly concerned, and even in cases where the determining causes appear to be physical, associated chemical factors may be proved to be operative.' 'In consequence of their structure hydrogels manifest an extraordinary development of (interior) surface, and consequently all those activities which are known as surface actions. . . . It cannot be postulated that these actions are purely physical in character. Certainly chemical influences are active in the formation of

absorption compounds, and it cannot even be stated that they are inoperative in the surface actions of other substances, such as graphite, charcoal, and fine powders, since Knoblauch has shown that the surfaces of many such bodies are by no means chemically inert.'

But in the development of his interesting generalisation Jordis stops short of the fibre colloids—in fact, devotes relatively little attention to the colloidal carbon-compounds.

No doubt these alternative provinces will be included in the immediate extension of the theory, and it will come to be recognised that cellulose is a more comprehensive type of colloidal matter than any other known substance.

Our own opinion is that the controversial aspect of the 'theory of dyeing' is the expression of the fact that we find it difficult to avoid applying molecular conceptions and criteria in a region of phenomena where the 'molecule' never is the reacting unit. We cannot expect to change our perspective by any partial study of new experimental matter. We can only expect to repeat previous experience in finding that conviction will result from the convergence of proofs from various apparently independent lines of research.

11.

ELECTROLYTIC PHENOMENA.

This discussion of the affinities of cellulose and their manifestation in the formation of 'absorption compounds,' leads directly to the consideration of the relationship of cellulose to electrical energy. This may conceivably involve a very large question, but for the present we confine ourselves to experimental results, proving that moist cellulose behaves as a conductor of the current, with associated electrolytic phenomena of a special character.

11 (*a*). We gave a preliminary account of such reactions in a paper which appeared simultaneously with our first volume

on 'Cellulose,' under the title 'Contributions to the Chemistry of Celluloses' (J. Chem. Soc. 1895, 433–451), which we may cite as shortly representing the point of view from which that volume was written. Under the sub-title 'Some Electrolytic Phenomena of Cellulose,' we first described experiments showing that moist cellulose acted as a conductor of current; secondly, we established the fact that, when a conducting circuit was completed by moist cellulose in contact with two metallic terminals, varying effects were obtained, which could only be explained as resulting from a species of electrolysis of the cellulose, an electrolytic strain under which constituent groups of the cellulose became chemically active.

The anode metal was attacked, the reactions with silver being specially marked. Gold and platinum were also attacked, Silver was retained in combination with the cellulose. Gold was in large part carried through the cellulose and deposited in the cathode, platinum to a still greater extent. An instrument was devised, described as an 'electrograph,' for demonstrating these effects, and will be found described in 'Nature' of June 20, 1905.

The subject has been more recently investigated by C. R. Darling, and an account of his researches is given in a paper on 'Experiments in Thin-film Electrolysis and a Proposed Application to Printing,' read before the Faraday Society, March 21, 1904. He confirms our results as regards the action on the anode metal, but extends our observations to the important complementary effects which are to be observed at the cathode. Mr. Darling has prepared for us a brief note on these observations, which we give in full:

11 (*b*). 'When a current of electricity is passed through a sheet of moist cellulose, a latent image of the cathode is retained in the surface layer which has been in contact with the metal or conductor used as cathode. The presence of the image can be readily detected by brushing the surface of the cellulose with a solution of silver nitrate, and afterwards with hydroquinone, when a sharply defined picture of the cathode is obtained in silver. Electrographs, or cathode pictures, may

be produced by this treatment in a sheet of paper many months after passing the current; longer contact with the reagents, however, being in this case required. The presence of salts in the cellulose does not prevent the formation of the latent image, which has been detected in a sheet containing a salt of lead after the lapse of five years. Of the possible explanations of the phenomenon, the most obvious, perhaps, would appear to be the presence of matter dissolved from the anode or cathode. This, however, is negatived by the following observations: (1) the latent image is present when carbon plates are used both as anode and cathode; (2) there is no tendency for the image to spread on keeping, even when the sheet is moist; and (3) the image resides in the surface film only, and cannot be detected on the under side of the thinnest sheet. The presence of hydrogen peroxide has been suggested as an explanation; but not only is it improbable that this substance would be formed at the cathode, but, in addition, a cellulose film containing a latent image may be placed in contact with a sensitised plate for a week without causing photographic action. The phenomenon is therefore entirely different from those investigated by Russell, and referred by him to hydrogen peroxide. The only direct explanation appears to be that the cellulose itself has been modified or strained by the current, so as to render the part in contact with the electrodes more active, chemically, than the remainder; thus showing, to some extent, the properties of an electrolyte.'

These reactions have been investigated rather as 'residual' phenomena, and in the discussion which followed the reading of Mr. Darling's paper the tendency of criticism was to reject the explanation put forward and substitute those based upon the actions of associated 'impurities.'

But in view of the general theory of the colloidal state which has directed our present treatment of the subject, we should regard these phenomena as essentially correlated with the amphoteric activity of the cellulose. Therefore, as the experimental results are clear in their indications, and the alternative hypotheses have been carefully examined and found

untenable, we are entitled to adopt the conclusions as a confirmation of the general theory.

It will appear that the investigations hitherto carried out have been concerned mainly in establishing the empirical facts; but in generalising their possible significance and bearing on the problems of constitution, a much wider field of experimental investigation is opened up.

If the 'cathode image' is the expression of a permanent stress set up in the cellulose complex, we should be able to ascertain the correlative chemical changes. If these should prove to be consistent with variations of constitution or configuration such as are determined by the actions of hydrolytic agents, we should have a definite clue to the labile equilibrium of the complex, which has been established by a purely chemical interpretation of these reactions.

11 (*c*).[1] Mr. Albert Campbell, of the National Physical Laboratory, has made a number of observations upon the electrical properties of structureless cellulose, as obtained in continuous masses from the decomposition of solutions of the xanthate (viscose). The specimens were prepared by ourselves and represented the approximately 'pure' cellulose (hydrate). We are indebted to Mr. Campbell, with the kind permission of Dr. R. T. Glazebrook, for the subjoined brief note of results in advance of the fuller publication:

'A number of specimens of pure cellulose in films and sheets of various thicknesses were tested for specific inductive capacity by Maxwell's method with quick periodic charge and discharge, the frequency being varied from 10 to 40 charges per second. In the ordinary air-dry condition the material was found to conduct like an electrolytic solution, showing distinct polarisation. When dried for several hours from 80° C. to 120° C. and tested at temperatures from 120° C. down to 20° C., the apparent capacity fell steadily with the tempera-

[1] Report received in course of printing, March 27, 1906.

ture. With long-continued drying the material became very brittle, and in that condition the specific inductive capacity became practically independent of temperature and its value was of the order of 7. These tests would be consistent with the assumption that except when in the dry and brittle condition the material may be described by the formula

$$m(\text{Cellulose hydrates}) + nH_2O$$

where $m+n=$a constant mass and n increases as the temperature rises. This is, in other words, a solution of cellulose hydrates in water, the hydration depending on the temperature, and dissociation equilibrium occurring at any fixed temperature.'

12.

ON THE CONSTITUTION OF CELLULOSE.

A. G. GREEN (Ztschr. f. Farb. in Textil. Chemie, 1904, 3, 97); C. F. CROSS and E. J. BEVAN (*ibid.* 197); A. G. GREEN (*ibid.* 309).

Ueber die Konstitution der Cellulose.

The above contributions comprise (1) a summary of points of evidence as to the constitution of cellulose, (2) a criticism of the constitutional formula proposed in (1), and (3) a rejoinder by the original author.

The substance of A. G. Green's review of the evidence may be shortly re-stated as follows:

12 (*a*). The accepted empirical formula $C_6H_{10}O_5$ has given place to one with a C_{12} molecule, in accordance with the observation of the formation of tri- and penta-nitrates. It is doubtful whether these esters are chemical individuals. The nitrate reaction is complicated by water-exchanges (hydration and condensation), and it is difficult to establish the exact relationship of the ester to the original cellulose.

It is assumed that cellulose is a compound of high molecular weight mainly on the ground that it is an insoluble colloidal substance. But the reasoning is here insufficient, for alumina and silica, although essentially colloidal, are represented by simple molecular formulæ.

Failing cogent proof to the contrary, the author adopts the simple formula $C_6H_{10}O_5$. This he proceeds to expand into a constitutional formula to embody the following empirical facts :

1. The highest nitrate has the composition of a trinitro-derivative $C_6H_7O_2\ (O.NO_2)_3$.

2. The highest acetate appears to be the triacetate ; the tetracetate, if obtained, is probably derived from a product of hydrolysis.

3. Cellulose combines with sodium hydrate, the product is decomposed by water, the cellulose being converted into a hydrate (mercerisation). This hydrate is more easily soluble than the original cellulose in the aqueous saline solvents, cuprammonium, and zinc chloride.

4. The compound of cellulose and alkaline hydrate reacts with carbon disulphide to form unstable thiocarbonates, from which cellulose is easily regenerated in the form of hydrate.

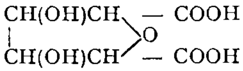
5. Cellulose does not react with phenyl-hydrazin nor with hydroxylamine. Although therefore not containing CO groups as such, it readily yields products so characterised, under simple hydrolytic treatment.

6. Cellulose is resolved by treatment with sulphuric acid into dextrose as the final product of the attendant hydrolyses.

7. By treatment with hydrobromic acid, cellulose is resolved directly into brom-methyl-furfural (Fenton).

8. By oxidising agents cellulose is converted into oxycellulose, a nearly related derivative of weak acidic character, which is decomposed by boiling dilute acids with production of furfural, and

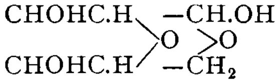
9. By boiling with calcium hydrate into iso-saccharic acid



and dioxybutyric acid (Faber and Tollens).

10. The cellulose nitrates are decomposed by the alkaline hydrates with formation of hydroxypyruvic acid $CH_2OH.CO.COOH$.

To summarise these facts the author proposes the constitutional formula



and discusses its application to the several typical reactions.

It is noted in conclusion that the formula can be readily adapted to the case of a more complex constitution—i.e. in the sense of a polymeride.

12 (*b*). The authors, without impugning the correctness of the deductions contained in the preceding paper, from the experimental data which are stated find it necessary to point out the entire inadequacy of this statement, and generally to show that any attempt to express the chemistry of cellulose in the terminology of molecular formulæ is in opposition to the obvious trend of the evolution of research in this province.

In regard to the narrower question of a possible formula giving expression to the reactions of cellulose, it is pointed out that the formula proposed by Green is hardly reconcilable with the fact that all the monoses are readily resolved by the alkaline hydrates with production of acid bodies of lower molecular weight, whereas cellulose shows an extraordinary resistance to the alkalis, even surviving 'fusion' at 180° (Lange). In this respect cellulose is not only far removed

from the monoses, but from the complex carbohydrates, such as starch, also containing no free CO groups. The C_6 reacting unit is further entirely incompatible with the evidences of the series of xanthates and the spontaneous passage of the C_{12} xanthate through the stages of C_{24} to C_{48}, both of which are well-marked though transitional equilibria (Ber. 1901, 1513).

It is further objected that a C_6 formula would have at least equal *à priori* justification in the case of starch. But the quantitative statistics of its various hydrolytic resolutions offer a sufficient evidence of actual complexity. Although there are no directly comparable decompositions of cellulose, those which have been studied reveal a complexity not less pronounced. Further, the regeneration of cellulose from the xanthate, traced through the stages of increasing aggregation, is a direct proof of a reacting unit of continuous and large dimensions.

It may be objected that the complexity here noted is the expression of physical properties. But the conception of the 'molecule'—and a simple molecule—is actually derived from physical measurements. It does not therefore seem justifiable to apply these conceptions and terminology in a region where obviously a quite different order of physical relationships obtains.

In regard to the number of OH groups in the cellulose unit, and the denial of the existence of a tetracetate (C_6), the authors do not admit that sufficient evidence has been brought forward as against their own quantitative study of the acetylation—in regard to yield and saponification values of the acetate. But an extension of their investigations to the acetosulphates has revealed the production of a well-defined mixed ester of the lowest empirical formula $4C_6H_7O_2.SO_4(C_2H_3O_2)_{10}$, in which the ratio $4C_6 : SO_4$ fixes a minimum reacting unit of $4C_6$ dimensions.

On the other hand, many of the typical reactions of cellulose may be perfectly well expressed by a C_6 formula; further, it is resolved by certain decompositions to C_6 carbohydrates (Flechsig, Stern) or their immediate derivatives (Fenton), and Green's formula is therefore a useful suggestion as to possible constituent groups. But a ketonic constitution is equally if not more probable.

In reference to Green's method of disposing of the objection based on the colloidal characteristics of cellulose and its derivatives, it is pointed out that the formulæ Al_2O_3, SiO_2 by no means represent the dimensions of the respective oxides. They are really 'valency' formulæ, based upon and derived from the study of other compounds of these elements. The question of the relationship of chemical function to colloidal aggregation is a problem of the future. In cellulose we have extensive evidence that the colloidal properties and structural characteristics of the substance itself and of its derivatives are essentially bound up with chemical constitution. Nothing illustrates this more forcibly than the typical technical methods of obtaining 'artificial silk,' which involve the widely divergent reaction series:

	Ester	Spinning stage	Regeneration of cellulose
Cellulose	$H_2SO_4 + HNO_3$	Collodion	Denitration
Cellulose	$NaOH + CS_2$	Xanthate solution	Spontaneous decomposition of NH_4 salt

The close coincidence of structural conditions under these most divergent conditions of chemical modification prove that the colloidal characteristics are not dependent upon *incidental* 'physical' factors, but the expression of fundamental properties—i.e. constitution. No subject of experimental inquiry is better calculated to impress the investigator with the essentially chemical factors involved in the colloidal state; the obvious

result of recent researches in this special field is to show that cellulose is a prototype of the structural colloids, and investi gations prosecuted from this comprehensive point of view may be expected to contribute to the progress of science generally.

12 (*c*). In the rejoinder to the preceding criticism, A. G. Green points out that it is not an essential, nor indeed important, part of his first communication to maintain a C_6 formula for cellulose; his object is rather to formulate the typical C_6 unit group. The criticisms, based upon the complex mixed esters and the relations of the xanthate series, do not affect the position of the constitution of the unit group, and the degree of complexity of the cellulose molecule—i.e. as to how many of the unit groups are united in the complex was left as an open question, with the remark that 'the assumption of a higher molecular weight for cellulose would merely involve oxygen linking of units of the given constitutional formula.'

On the special points at issue it is observed that the resistance to the action of alkalis is not at variance with the formula, which represents a species of interior aldehyde-ester or acetal. The acetals as a class are much more resistant to alkalis than the aldehydes from which they are derived. On the question of the existence of a tetracetate the author has analysed specimens of the product reputed to have this composition—using the acid method of saponification proposed by A. G. Perkin (Proc. C. S. 1904, 171), and obtained results in close agreement with the theoretical numbers for the tri-acetate. It is also to be observed that the aceto-sulphate formulated in (2) represents the esterification of 12OH group in the $4C_6$ unit; therefore in the ratio of the tri-acetate. As against a ketone formula it is objected that cellulose does not react with phenylhydrazin or hydroxylamine; and further, that its latent aldehydic groups are readily brought into evidence under a variety of hydrolytic treatments.

The objection that the formula would equally apply to starch is met by the fact that starch and cellulose show a characteristic difference in their behaviour to hydrobromic acid (Fenton, J. Chem. Soc. 1901, 361), cellulose yielding a large proportion of brom-methyl-furfural, starch but little. The formation of this condensation product was especially taken into account by the author in the formula proposed.

* * * * * * *

We have noted these contributions at some length as they are typical of the two opposite points of view from which the problem of the constitution of the celluloses may be approached.

Since the present work is written from the point of view which underlies our criticisms contained in the above article (2), it would be mere repetition to further discuss the particular point. We make two observations in concluding this notice :

1. Green's formula may perfectly well apply to constituent groups of cellulose, or may represent those groups in particular phases of decomposition of the complex. The formulation is novel, and of course well grounded; it is therefore deserving of attention ; but

2. It is an entirely inadequate representation of the essential characteristics of cellulose as a chemical individual, with associated physical properties which are inseparable from its constitution. This, which is the general basis of our criticism, Green does not refute nor discuss. We may presume that he allows the weight of our contentions on the general question, as we acknowledge the value of his contribution on the particular issue.

B. Reactions of Decomposition.

From reactions of synthesis, generally involving the reactivity of cellulose *as* cellulose, we pass to reactions of resolution, in which the cellulose is progressively broken down.

13 (*a*).

THE SO-CALLED 'HYDROCELLULOSE.'

A. L. STERN (J. Chem. Soc. 1904, 85, 336).

The purpose of this communication is indicated in the opening paragraph, in which the author points out that all kinds of cellulose under the action of certain agents lose their tenacity and become friable. This is usually attributed to their conversion into 'hydrocellulose,' to which Girard assigns the formula $C_{12}H_{22}O_{11}$. The author's experiments are, however, at variance with the statements of Girard (Compt. Rend., 81, 1105; 88, 1322; Ann. Chem. Phys. 1881, 24, 337).

He states that his 'attempts to prepare hydrocellulose by the action of sulphuric acid (1145 sp.gr.), and by the action of cold moist hydrochloric acid on air-dried cellulose, proved unsuccessful.' He therefore adopted the plan of boiling with dilute acids—e.g. 5 p.ct. H_2SO_4. The following effects were established: The conversion into a friable powder was attended by loss of weight, 2 to 4 p.ct. The product again loses weight when the process is repeated. The soluble products of successive treatments were characterised as *d*-glucose. The friable residue was analysed and gave results agreeing closely and uniformly with the empirical formula $C_6H_{10}O_5$. The hydrate formula $C_{12}H_{22}O_{11}$ assigned by Girard to his various

products the author considers to be based on errors due to the preparation of the material, which may have contained sulphuric acid in some cases, or water not expelled at 35° to 40°, the temperature at which he dried his specimens.

The author concludes that under the action of hot dilute acids there is no formation of hydrocellulose; the cellulose is partly hydrolysed with the production of soluble products—probably *d*-glucose. The residue does not differ in elementary composition from the original cellulose, and its disintegration is due to the fact that certain portions of the fibre are more easily attacked than others, and as a result of their solution and removal the whole fibre falls to pieces.

* * * * * * *

The above communication was criticised by ourselves in a paper which, on account of its brevity, we reproduce in full.

13 (*b*).

HYDROCELLULOSE.

C. F. CROSS and E. J. BEVAN (J. Chem. Soc. 1904).

The recent contribution of A. L. Stern (this vol., pp. 336–340) bearing the title 'The so-called hydrocellulose' is based on experimental matter of obvious value, which may be taken as being beyond criticism, but the author's interpretations appear to us to be somewhat at variance with accepted facts and liable to misconstruction.

This appears in the title itself, which must be read in the light of the context supplied by one of the concluding paragraphs, where the author says:

'It is evident . . . that when cellulose is exposed to the action of hot dilute acids there is no formation of hydrocellulose. . . . The cellulose residue . . . does not differ in elementary composition from the original, but has been

converted into a fine powder. . . . A microscopic examination . . . shows that the disintegration is due to the fact that certain portions of the fibres are more easily attacked than others, and when these portions are converted into soluble products the whole fibre falls to pieces.'

We do not propose to discuss the statements in detail, but with all possible brevity to emphasise some antecedent facts which, although of critical importance in this connection, have apparently been overlooked.

(1) The author's criticisms of the work of A. Girard are scarcely justified, because the three methods for the production of the typical hydrocelluloses carefully described by the French chemist ('Mémoire sur l'Hydrocellulose et ses dérivées,' Paris, 1881) are in no case followed.

(2) The question as between an empirical formula $C_{12}H_{20}O_{10}$ or $C_{12}H_{22}O_{11}$ for the products described by Girard as the typical hydrocelluloses is therefore not raised by the fact that the author has obtained, under other conditions, residues which have the empirical composition $C_{12}H_{20}O_{10}$ of the original cellulose.

(3) On the other hand, we submit that these residues are constitutionally different from the original cellulose. They are attacked by dilute alkaline solutions, are largely soluble in 15 to 20 p.ct. caustic soda solution, are oxidised by Fehling's solution, and generally show differences in the reactivity of the typical carbonyl and hydroxyl groups. Their behaviour towards nitric acid, acetic anhydride, and esterifying reagents generally differs from that of the original cellulose, and the properties of the corresponding derivatives are also different.

Girard studied this part of the subject in detail, in regard to the typical hydrocelluloses, and his results have been frequently confirmed.

(4) The main point which Stern appears to overlook is that structure in the celluloses is bound up with chemical composition and constitution. The structural properties of cellulose and hydrocellulose persist in their esters, and also through a cycle of reactions such as is involved in the conversion into

xanthate and the regeneration of the cellulose (or hydrocellulose) from this condition of combination.

This very important point has closely engaged the attention of investigators, and considerable positive evidence has already been accumulated showing that the structural properties of cellulose are a function of the actual molecular aggregate taken in the chemical sense.

Incidentally we would emphasise the point that it is at present easily open to chemists to settle any question as to chemical changes in cellulose, independently of structure, by operating on the homogeneous, structureless forms of this compound now available.

Without extending our criticism to lesser details, we conclude that the sub-group connoted by the term 'hydrocellulose' remains unaffected by Stern's investigations save as regards his useful contribution of new matter.

Finally, in order to illustrate the actual state of our knowledge of the sub-group in question, we may point out:

That the normal cellulose (anhydride) is chemically labile, as it is a structurally plastic aggregate, occupying a middle position between the two extremes, determined by treatment (*a*) with alkali hydroxides, (*b*) with halogen hydracids, both in presence of water.

These extremes are both chemical and structural; under (*a*) the carbonyl groups show no reactivity and may be assumed to occupy a ketonic or cyclo-ketonic position in the aggregate; under (*b*) they become distinctly aldehydic, and in fact the aggregate is partly resolved with the production of free aldoses.

Structurally, the maximum of integration is attained under (*a*), whilst the maximum of disintegration is reached under (*b*).

This very wide range of variation falls mainly within the limits of hydroxyl reactions; the direct effects produced are those of hydration and hydrolysis, with the complementary phenomena of reversion.

In the case of the alkali hydroxides, the reactions, including the phenomena of 'mercerisation' are chiefly those of hydra-

tion, some hydrolysis probably accompanying the effects, but without resolution of the cellulose to soluble forms, at least in the case of the normal cotton cellulose.

With acids, it appears that the hydrolysis which occurs and which, in fact, proceeds to the extreme limits—since the cellulose is partly resolved into the simple aldose—is accompanied by effects of reversion. The substances described by Stern have the character of reverted products.

In either case, it is obvious that the empirical composition of a final residue throws but little light on the changes it may have undergone. In many such reactions the alterations in composition are fractional, but it is none the less evident that profound constitutional changes occur.

A terminology for the brief expression of these classified effects must for the present remain on a conventional basis.

It would be convenient to retain the terms which have hitherto been current—namely, hydracellulose and hydrocellulose. The former might be limited to the products of the action of alkalis on cellulose, which are certainly hydrates; hydrocellulose, on the other hand, might be applied to the products of acid reactions, which are certainly hydrolysed, although in many cases showing the empirical composition of the original anhydride.

The latter have many properties in common with the 'hemi-celluloses,' a term which is useful in designating a group of natural, mostly cellular, celluloses, which are distinct from the fibrous celluloses in chemical constitution as well as in structure and function in plant life ('Cellulose,' Cross and Bevan, p. 87). This term might very well be extended to include the hydrocelluloses, if the suppression of the latter designation be considered advisable.

Whatever terminology may be finally adopted, it is important that in the meantime the empirical facts should be kept clearly expressed, and our purpose in this contribution is to prevent the confusion of issues which is likely to result from the theoretical views set forth in the paper now under discussion.

14.

ON STARCH, GLYCOGEN, AND CELLULOSE

ZD. H. SKRAUP (Monatsheft für Chemie. 1905, 26, 9, 1415).

Ueber Staerke, Glycogen, und Cellulose.

The molecular weights of the polysaccharides, though of importance, have never been fixed, even approximately. The usual physical methods are obviously inapplicable and the chemical methods have given results which are quite certainly too small. A new method appears to promise in the action of acetic anhydride saturated with HCl. This reagent was shown by Bodart to act on lactose and give a body of formula $C_{12}H_{14}O_3(OAC)_7Cl$, and similar actions have been established by Foerg for maltose, and by Skraup and Koenig for cellobiose.

The author expected, therefore, similar synthetical reaction with starch—i.e. without resolution; in such case the determination of the chlorine would be a criterion of purity, and a measure of actual molecular weight. It was possible, on the other hand, that the action might simultaneously take the course of resolution or decomposition, as in the case of acetic anhydride and sulphuric acid, the resulting esters being derivatives of products of decomposition of the original carbohydrate.

In collaboration with the author, F. Menter has shown experimentally that by acting on starch with eight times its weight of anhydride, saturated at $-20°$ with HCl, for the prolonged period of 4 months at ordinary temperatures, it was converted into acetylchlorglycose. After 2 months it gave a body resembling acetylchlormaltose; but after 14 days, as a main product, the compound $C_{74}H_{99}O_{49}Cl$, with constant chlorine of 1·92 p.ct., and which can be converted into the erythrodextrine, $C_{36}H_{62}O_{31}$. The acetate with benzene by

E.P. method gave results for molecular weight lying between 1,700 and 2,000 (1,806 calculated). Under other conditions other products were obtained.

Working in collaboration with the author in further investigation of this series of products, H. Sirk found that the first product was a body with constant chlorine percentage 0·2 %, from which a 'soluble starch' could be regenerated; for the ester the molecular weight 13,230 was calculated from experimental observations.

E. von Knaffe obtained from glycogen a body with contant chlorine 0·15 p.ct., molecular weight 23,630. From this a glycogen was regenerated with molecular weight 15,350.

E. Geinsbergen has carried out experiments on cellulose (filter-paper). After 48 hours' action the chloracetyl compound was obtained which represented the cellulose molecule $(C_6H_{10}O_5)34=5{,}508$. Bumcke and Wolfenstein (Ber., 32, 2507) found 1,944. A. Nastukoff (Ber., 33, 2243) found 6,480. After 14 days' action at the ordinary temperature, he obtained $C_{26}H_{35}O_{18}Cl$, identical with acetochlorcellobiose.

* * * * * * *

This communication might have a critical value in deciding as between the two opposite theories of the constitution of cellulose—namely (1) that which regards it as a polymerised complex of hexose groups, and (2) the view to which we find ourselves impelled by a more general consideration of the activities of cellulose.

The reactions investigated by the author are, of course, under anhydrous conditions, and they are really comparable with the conditions under which Fenton succeeded in converting cellulose directly into furfural derivatives.

It is interesting to note, however, that even under these conditions the time-factor is of evident importance, and that there is a gradual resolution of the aggregate.

It is also evident that the criterion adopted by the author, that is, the amount of chlorine combining, is justified by the results obtained.

Further, the very high molecular weights deduced as correlative to the chlorine combining appear to be justified as conclusions from the experimental results. This mode of attack is certainly to be taken into account in any general view of the constitution of cellulose, and we look forward to the author's further communications.

15.

INVESTIGATIONS OF ASSIMILATION IN HERBIVOROUS ANIMALS.

BERICHT VON O. KELLNER (Landw. Vers. Stat. 1900, 53, 1, 474).

Untersuchungen ueber den Stoff und Energieumsatz des erwachsenen Rindes.

This is a detailed account of elaborate investigations of the total physiological effects of typical fodders, fodder-constituents, and feeding materials generally, the following being more particularly studied :

Clover proteids, earth-nut oil, starch, *straw cellulose*, molasses, meadow hay, oat straw, and wheat straw. The especial interest of the work in its connection with our subject lies in the fact that an artificially prepared straw pulp (cellulose) was included for investigation. This pulp was prepared by treating rye straw under the following conditions : for 1,000 kg. straw, 2,070 litres of a solution containing per litre 55 grms. NaOH, 20 grms. Na_2CO_3, and 22 grms. $Na_2S + Na_2S_2O_3$, treated for $3\frac{1}{2}$ hours at 7 atmospheres steam-pressure, afterwards exhaustively washed till free from soluble matter. Such a product

may be taken for the purposes of the inquiry as a pure cellulose.

It would take us far away from the scope of this work to deal with this important contribution in any detail. We must assume acquaintance with the author's experimental methods and confine ourselves to a brief notice of the final conclusions. These are given in the form of quantitative comparative tables in the concluding section, setting out the values obtained for physiological efficiency (Nutzeffekt) (*a*) Under the condition of no increase of weight of the animal, (*b*) in relation to increase of weight.

(*a*) In arriving at the ratio of energy utilised in digestion and assimilation to the total available energy of a food, the sources of loss usually taken into account are those of the excreta, solid and liquid, and of the methane and hydrogen resulting from intestinal fermentations. The latter is found, however, to be of small moment and is neglected, as well as the minor thermal changes involved in hydration, hydrolysis, &c., of the food constituents.

The following are the numerical results under this head :.

—	Calorific value per 1 grm.	Calorific value lost in excreted		Total loss	Physiological efficiency per 1 grm. digested
		Urine	Methane		
		P.ct.	P.ct.	P.ct.	
Clover proteid .	6148	19·3	—	19·3	4958
Earth-nut oil .	8821	—	—	—	8821
Starch . .	4183	—	10·1	10·1	3760
Straw cellulose .	4247	—	14·0	14·0	3651
Molasses . .	4124	3·6	12·3	15·9	3462
Meadow hay .	4425	8·2	11·5	19·7	3553
Oat straw . .	4513	4·7	12·2	16·9	3747
Wheat straw .	4470	5·6	20·0	25·0	3327

It may be noted that the numbers for the typical carbohydrate foods, starch, cellulose, and straw, are nearly identical.

(*b*) Of the total physiological efficiency the proportion available for increase in body-weight varies between the limits of 17 and 70 p.ct. The following are the percentages deduced as available:

	P.ct.
Clover proteid	45·2
Earth-nut oil	56·3
Starch	58·9
Straw cellulose	63·1
Molasses	68·3
Meadow hay	40·2
Oat straw	37·6
Wheat straw	17·8

l the following table gives the complete view of the utilisation of the energy of the food constituents actually digested:

—	Losses of energy of digestible constituents				Energy equivalent of flesh and fat formed
	In urine	Methane fermentation	Other processes	Total	
	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.
Clover proteids	19·3	—	44·2	63·5	36·5
Earth-nut oil	—	—	43·7	43·7	56·3
Starch (meal)	—	10·1	37·9	47·0	53·0
Straw cellulose	—	14·0	38·7	45·7	54·3
Molasses	3·6	12·3	26·8	42·7	57·3
Meadow hay	8·8	9·0	47·0	64·8	35·2
Oat straw	4·7	12·2	51·9	68·8	31·2
Wheat straw	5·6	20·0	61·2	86·8	13·2

On these values the author particularly remarks as follows: The straw cellulose freed from lignone constituents has a nutritive value, as flesh former, equal to that of starch. In comparing the numbers for straw cellulose with those for the untreated straws with special reference to the fate of the furfural-yielding components (furfuroids), it is concluded that the latter are fat formers and are equal in value to cellulose and starch. It is also concluded that the cellulose is easily digested and in such a way as to prevent the consumption of proteids for respiratory needs, and therefore render them

available as flesh formers. Lastly, attention is specially directed to the fact that the straws in their raw state have a very much lower efficiency than their component groups; and in particular the separated cellulose, as such, has a much higher actual feeding value than when taken into the organisms in its naturally occurring form.

* * * * * * *

On this communication we make the following remarks:

There is a particular interest in the facts revealed with regard to cellulose. According to the ordinary estimate of digestibility, the cellulose might be presumed to be very much inferior in general value to the straw from which it is prepared. As the author observes in a more particular discussion of these results, wheat straw with 58·6 p.ct. 'crude fibre' is lowest in the sense of 'efficiency'—i.e. as a flesh and fat producer—whereas the cellulose artificially prepared, with 82·[illegible] p.ct. 'crude fibre,' is of efficiency equal to that of a farinaceous meal.

In regard to the factor of actual digestibility, on the other hand, these numbers are of no indicative value, for the proportions arrived at in the investigations and given on p. 302 of the publication are:

—	Percentages digested		
	A	B	Mean
Total organic matter .	89·1	87·6	88·3
Extractive matter . .	77·8	80·7	79·2
'Crude fibre' . . .	97·0	94·7	95·8

In the case of this 'artificial' cellulose, therefore, there is not only a high 'efficiency' or feeding-value, but an unusually high digestibility. In dealing with the causes of differentiation from the original straw, the author mentions the two which are more evident, the altered physical condition by resolution

into ultimate fibres and cells, and the elimination of the relatively indigestible 'lignone and incrusting matters.'

Admitting these factors as contributory, they by no means exhaust the probabilities from the standpoint at which we have arrived. We cannot overlook the constitutional changes which accompany the isolation of the cellulose. We may regard a lignocellulose, as in the straw substance, as a species of ester, and the action of the alkaline mixture used for 'pulping' the straw as a saponification with secondary actions due to the sulphides used partly of deoxidation, partly of direct synthesis with sulphur groups. But the separated cellulose is not related to the original lignocellulose at all in the same way as, for instance, glycerin to the glycerin ester, from which it is obtained by saponification. As a matter of experimental fact, a glycerin separated by an alkaline process is identical with glycerin obtained by the action of acids. But not so cellulose. The cellulose obtained from wood by the action of bisulphites is a different body from 'soda wood pulp' or cellulose. And further, the ligno-celluloses are not resolved by the purely hydrolysing action of acids. A further condition requires to co-operate with a specific action on the unsaturated ketonic groups of the lignose.

Cellulose as a 'solution complex' or 'intrinsic electrolyte' must undergo a constitutional modification in response to the action and influence of any and every extrinsic electrolyte with *which it is in 'solution contact.'*

The results of this extensive physiological investigation may both confirm and extend the theoretical views contained in the earlier sections of this treatise.

Chemists may be a little 'shy' of the statistical methods of the physiologist, but this arises from a sense of vagueness or indefiniteness when detached from the familiar conceptions of ultimate molecules and molecular reacting groups. But the statistical method is obviously sound and necessary; the indispensable complement of molecular methods and conceptions in a region where the molecule is indissolubly merged in the aggregates which are the actual objects of investigation.

The errors of physiological methods are, no doubt, relatively large, and there are complications which arise from ignorance and necessary want of control of the vital factors involved. But as every scientific method, and indeed every theory, is justified by its capability of contributing to the advance of exact knowledge, it is evidently gratuitous to criticise physiological methods from any other standpoint.

The methods belonging to cellulose chemistry occupy an intermediate position. The statistical method is in this case also the necessary complement of the stoichiometrical, and there is no control of the intermediate phases of reactions, for the reason that there is no knowledge of the actual conditions, material and physical, of the colloids in reaction.

It appears therefore that there is much common ground, both of method and material, as between the physiologist and the investigator of the organic colloids. This may be self-evident, but it is none the less true that the region remains to all intents and purposes unexplored.

As a practical illustration arising out of the investigations under discussion, if the objective of these investigations were diverted to 'cellulose' the following problems would arise for investigation :

1. The relative 'efficiency' of straw cellulose prepared (*a*) by the bisulphite process, (*b*) by the alkaline process.

2. The relative 'efficiency' of straw cellulose (containing 25 p.ct. furfuroids) and a wood cellulose (containing 6 p.ct. furfuroids).

3. The fate of a structureless cellulose as regenerated from 'viscose' in the digestive tract of the herbivoria, and its quantitative effects in reference to digestibility and 'efficiency.'

The results of such investigations should afford an important commentary on the classification of the celluloses previously adopted ('Cellulose,' ed. 1903, 78-87). The digestive tract of the herbivora is evidently provided with the conditions for both proximate and ultimate resolutions of cellulose When the proximate resolution is in the ascendant, the cellulose appears to have a similar physiological function to that

of starch. This has only been proved in the case of one cellulose, and of that cellulose prepared by a particular process. A comparative investigation of other types would establish some important constitutional relations.

In regard to the destructive ferment resolutions with production of marsh gas, these may be provisionally assumed to be of the type established by the investigations of Omelianski, in which the complementary products are butyric and other fatty acids.

A more detailed separation of these factors would be possible, and especially so if the inquiry were extended to other types and groups of herbivorous animals.

More definite contributions to the general theory of cellulose constitution would result from the study of cellulose derivatives, such as the products of the extreme action of alkalis (mercerisation) and acids ('hydrocellulose'). We have, however, no intention to anticipate these investigations, and the purpose of this superficial forecast is rather to emphasise the intimate connection of our subject with an important branch of physiology, and the certainty of reciprocal advantage to both from a more definite cultivation of the region common to both.

16.

THE DESTRUCTION OF VEGETABLE CELL-WALLS—CELLULOSE FERMENTATION.

W. Omelianski (Handb. d. techn. Mykologie (F. Lafar), pp. 245–268).

Die Zersetzung der Baustoffe der Zellwaende der Pflanzen—Die Cellulose-Gaehrung.

The author gives a brief historical survey of the earlier observations and investigations of chemists and biologists, E. Mitscherlich (1850), Trécul (1865), van Tieghem (1877), Prazmowski (1879).

More definite results come from the researches of Popoff, Tappeiner (1880), and Hoppe-Seyler (1886), which were chiefly directed to the chemical factors and gave general indications of the main products—viz. as gaseous end-products, methane and carbonic anhydride ; and as intermediate products, acetic and butyric acids.

Parallel with these investigations the subject was attacked by agricultural chemists in reference to the changes taking place in farmyard manure when stored in masses, but beyond establishing the production of methane, and general statistics of the destruction of the straw substance, these researches did not contribute definite results as regards cellulose.

It was reserved for the work of Omelianski to establish a well-defined method of observation leading to exact results. This author's researches were confined to the normal celluloses, employed in the form of Swedish filter-paper. The cellulose was placed in flasks which were filled with a nutrient solution containing, per litre, potassium phosphate 1 grm., magnesium sulphate 0·5 grm., ammonium sulphate 1 grm., and a trace of sodium chloride.

The bacteria were introduced in an inoculating liquid obtained from horse-dung or river mud. Chalk was present in excess throughout the period of fermentation. A temperature of 34° to 35° was found to be the optimum.

A general preliminary investigation established two types of fermentation, the one characterised by the production of hydrogen, the other by the evolution of marsh gas, as the main gaseous product. Since the incubation period required for the former is much shorter, and the bacilli are sensitive to a temperature of 75°, it is easy to inhibit this type and procure the hydrogen fermentation by heating the inoculating fluid for a short time at that temperature.

The following are the quantitative results obtained in typical cases of either fermentation:

Hydrogen Fermentation.

	grms.	Products.	grms.
Cellulose taken . .	3·4743	Fatty acids . . .	2·2402
,, residual . .	0·1272	Carbonic acid . . .	0·9722
		Hydrogen . . .	0·0138
,, fermented .	3·3471		
			3·2262

The fatty acids consisted of acetic and butyric acids in the molecular ratio 1·7 : 1·0. The fermentation period in this experiment was 13 months.

Methane Fermentation.

	grms.	Products.	grms.
Cellulose taken . .	2·0815	Fatty acids . . .	1·0223
,, residual . .	0·0750	Carbonic acid . . .	0·8678
		Methane . . .	0·1372
,, fermented .	2·0065		
			2·0273

The fatty acids consisted of acetic and butyric acids in the molecular ratio 9 : 1. The fermentation period in this experiment was $4\frac{1}{2}$ months.

* * * * * * *

From these investigations we are unable to draw any conclusions as to the intermediate products of resolution. We have previously had the opportunity of contributing material for the similar investigations of A. Macfadyen and F. R. Blaxall, the results of which are published under the descriptive title 'Thermophilic Bacilli,' J. Path. Inst. 1894 and Trans. Jenner Inst. (2), p. 162. The material which we supplied was a typical range of fibrous celluloses and also structureless cellulose (hydrate), all of which were attacked and resolved, in periods of from 7 to 21 days, under the conditions of these authors' experiments. We were unable to detect any

intermediate carbohydrate products in the solutions which we examined.

These investigations have been resumed, and we have again had the opportunity of co-operating in regard to the supply of experimental material; also of confirming the observations of Omelianski (*loc. cit.*) as to the visible evidences of the progressive destruction of the cellulose in the case of the fibrous celluloses. The microscopic observations o this observer are photographically recorded, and they will be found to faithfully represent the structural changes which the celluloses undergo.

The only point which calls for particular remark is tha the structural changes indicate a localised attack of the organisms, which implies that the breakdown of the cellulose requires actual contact with the bacteria. This interpretation is also consistent with the time-factors of these fermentations and the general absence of soluble carbohydrate products It is, however, impossible to affirm that an intermediate stage of solubilisation, as a result of enzyme action, does not occur Attention is being especially directed to this point in the further investigations now in progress, as well as to the more specific control of the biological features (Macfadyen).

Pending the results of these developments, we must accep the inconclusive position as to the actual mechanism of the process. So far as the evidence has accumulated, it is con sistent with the view that, as a hydrated colloid, cellulose pre sents the characters of a dissolved compound of which the component groups are in the reactive state; therefore tha previous conversion into 'soluble' products, as ordinarily understood, is not a necessary preliminary to destruction by the ferment organism.

It is of interest in concluding this survey of research work, to reduce our conclusion to a short but comprehensive summary.

Have we any alternative to offer to the views which will be

found formulated in the standard text-books? It is, of course, generally true that research in any field impresses the worker with the inadequacy of antecedent accounts of any group of phenomena, such as are to be found in the text-books. The didactic method rather implies the legal formula of completeness—that is, it affects the statement of facts in the sense of 'the truth, the whole truth, and nothing but the truth.' And this appears to be justified in many sections of the science where the total synthesis of compounds is taken as the evidence of complete knowledge. In many provinces also, the development and refinement of experimental methods have enabled investigators so exhaustively to penetrate those relationships of form or structure, which we express in the term 'constitution,' as to beget the conviction that the formulæ which express the relationships are a complete representation of the ultimate facts. We need only cite the evolution of 'stereology,' more especially that branch of it which has given us a complete account of the isomeric sugars—monoses—to show what we have to recognise in the general progress of exact knowledge. At the same time it is precisely in the same field that the limitations of this penetration into the 'actualities' of matter are quickly apparent, for with the comprehensive knowledge of the 'constituents of cane sugar,' the constitution of cane sugar itself is still unsolved; and with the more complex members of the carbohydrate group, the problematical elements of 'constitution' multiply in proportion to complexity of proximate composition.

It is a fair inference that other constitutional factors are introduced in the equilibrium of these more complex members of the group, and have to be reckoned with in attacking these unsolved problems. We may presume that the first indications will be furnished by the reactivities of the monoses in aqueous solution. We note the following points:

1. The typical CO group is labile, and the presence of the alkaline hydrates—i.e. of OH ions—raises its 'mobility' to the point that typical monoses are constitutionally interchangeable—e.g. dextrose, levulose, and mannose.

2. With increase of the OH ions and prolonged action there is a rupture of the C_6 nucleus; a complex of products result, the general feature of the resolution being an electrolytic migration.

3. With non-oxidising acids there is a series of decompositions very complex in character, but with similar general characteristics.

4. Most characteristic, of course, are the decompositions determined by ferments, which are in an important sense a property of the carbohydrates in the sense of a function of their constitution. We must not overlook the fact that in these effects the influence of stereoisomerism or 'configuration' are operative as modifying factors, but it is equally obvious that the general character of the decompositions is that of an interior electrolytic migration.

5. In various synthetical reactions with bases, and in crystallising with electrolytes, the monoses exhibit properties which are not revealed by their constitutional formulæ; though, of course, there is no inconsistency between such furmulæ and this group of reactions which they fail to indicate. If, then, the monoses in aqueous solution are electrolytes in the indicated sense, we have to inquire into the probable influence of this property in determining the constitution of the polyoses. It must be admitted that the present tendency is to assume for the entire carbohydrate group the comprehensive incidence of the molecular formulæ—i.e. of the factors of constitution (and configuration) which they connote. In other words, that the 'polyoses,' including starch and cellulose, are in effect nothing more than multiples of the monose unit, these units

essentially persisting in the complex, which merely introduces the additional but subordinate factor of linking by oxygen bonds. This, however, is hypothesis current in default of any positive alternative; hypothesis in the sense that it begs the entire question of the associated physical properties of these compounds. It assumes also that these 'organic bodies,' in the sense of vital products, retain no characteristic impress of the conditions under which they originated.

In general opposition to this view, chemists will be quite prepared to take up at least the agnostic position, recognising the primary fact that no molecular formula is finally justified, except by such physical measurements as fix the dimensions of the unit. They will then admit that, to emerge from this position, a working hypothesis is necessary, and that that hypothesis is most acceptable which formulates the greatest number of experimental questions. This in our opinion is furnished by giving full value to the physical properties of starch and cellulose as typical colloids, and applying to their investigation the general considerations which apply to the entire group of colloids, inorganic as well as organic; and chiefly that the colloidal state is not merely the accidental or incidental attribute of 'large molecules,' but a condition of matter determined by chemical factors—that is, by chemical functions, by valency and intrinsic energy or potential.

Thus we have found in the course of the present inquiry:

1. That the solid state of cellulose is continuous with that of its solution; there is no break in passing from one to the other, as in the case of compounds which crystallise.

2. Cellulose, in presence of water, is an electrolyte; it passes the current without decomposition, undergoes interior changes, and manifests a 'polar' activity. It does not revert to the original condition when the current ceases to pass. We have hence defined its electrolytic characteristics as 'intrinsic.

3. The presence of active ions in the fibre colloids, of which cellulose is a prototype, affords a consistent explanation of the phenomena of dyeing, involving a 'coagulation' stage, by interaction of ions of opposite electro-chemical function; and a stage of osmotic penetration of the fibre colloid, also facilitated by differences of potential, and in many cases attended by demonstrable ionisation of the colouring matter taken up.

4. The solutions of cellulose in aqueous solvents are the result of its amphoteric constitution; the solutions result from the reciprocal interaction of groups of opposite electro-chemical function.

5. Cellulose in contact with H and OH ions is continuously modified, both in chemical function and in structure; the modification is a function of the intensity of the action and its duration. Even when insoluble in the solution of the electrolyte, the cellulose is, nevertheless, in 'solution contact' with the active groups. The interpenetration is of the nature of that of two solutions perfectly miscible.

6. Cellulose is resolved by specific ferment actions.

7. Cellulose reacts synthetically to form esters and the reactions have continuous quantitative characteristics. There are no breaks marking 'molecular' stages, and the products which may be and doubtless always are mixtures, are not resolved by solvent fractionations as in the case of crystalline derivatives. The limiting stages correspond with the stoichiometrical ratios of the interacting unit groups, and vary with the chemical functions of the combining negative groups. Cellulose in these relationships is not less, and in some cases is demonstrably more, reactive than the simpler carbohydrates.

In these reactions it maintains its structural characteristics unaltered, or, if previously modified, as by conversion into hydrocellulose, the modification persists in the ester stage.

By saponification or spontaneous decomposition there is reversion to 'cellulose,' and in many cases the cycle, though marked by reactions of considerable intensity, is completed with only fractional changes of weight.

These are the more important facts to be summarised in a constitutional formula, if such were possible.

If we revert for a moment to the consideration of the conditions of origin of cellulose, we must conclude that the plant-cell has not synthetised monose groups as such into a complex multiple or polymeride. Having regard to the extreme sensitiveness of the monoses in aqueous solution, it is not to be supposed that they remain unresolved within the sphere of activity of the cell. On the other hand, the fact that the celluloses are resolved by specific acid treatments to monoses would imply that the actual component groups are ionised residues of the monoses. This view is not without its *à posteriori* evidences; these have indeed been categorically stated in the preceding pages. It is considerably strengthened by the inclusion of cellulose in the arena of investigation of the colloids as a class, by regarding cellulose as a typical representative of the colloidal state of matter and its properties in reaction as depending upon physical conditions specifically different, though not distinct, from those which determine crystallisation.

If this is conceded, two consequences result. First, that molecular constitutional formulæ are inapplicable to the celluloses; secondly, that progressive research must be based upon dynamic methods of the general type applicable to *solutions*.

As workers in this field we may say that these alternative views continually provide consistent explanations of phenomena which otherwise would be referred to the unrelated idiosyncracy of a chemical individual; but, more important still, they have suggested numerous directions of fruitful

investigation. For the present we must be content to develop the experimental subject-matter on the lines of these later researches, in close association with the most advanced movements of molecular science. The purpose of this essay is to aid in putting the subject in this, which we think will be recognised as a more comprehensive perspective.

SECTION III

TECHNICAL PROGRESS

THE period 1900–1905 has been marked by considerable activity in the development of the cellulose industries; but we are not aware of any movement which can rank as a 'departure' in this branch of technology.

In the long established staple industries involving chemical processes of preparation or treatment, such as textile bleaching, dyeing and printing, paper-making and the preparation of paper-makers' raw materials (celluloses), the only noteworthy feature is the general expansion and the increased perfection of method. In the wet spinning of short cellulose fibres by the processes known as the Kellner-Turk and Kron systems respectively, there has been a notable industrial development, and the present output of these cellulose yarns is estimated to be from 5 to 10 tons per day.

In the 'artificial silk' or 'lustracellulose' industry, the developments have been phenomenal. In the year 1899 the product was still regarded as an industrial curiosity, with a probable if problematical future. In 1900 it had vindicated for itself an unassailable position as a textile, and in the present year (1906) it has reached such a position that the estimated daily output in Europe is 7,000 kilos., increasing to 9,000 by the end of the year. A noteworthy feature of this advance in production is the correlative fall in selling-price, which may be estimated, on mean figures, at from 35 to 20 francs per kilo., say from 13*s*. to 7*s*. per lb. In the present deve-

lopments three systems are competing, the collodion process (Chardonnet-Lehner), the cuprammonium process (Pauly), and the viscose process (Cross and Bevan–Stearn–Topham). The final industrial equilibrium as between these systems on the one side, and the adjustment as between these artificial silks and the natural silk on the other, is a subject for speculative opinion, as well as for a judgment based upon the ultimate factors which are technical—that is, scientific. It is to be noted that the demands made upon the artificial silks in point of fineness and uniformity are increasing in severity, and a large percentage of the present production is within the limits of fineness represented by a thread of 110 to 130 deniers. This is already a large advance upon the range of 160 to 220 deniers, which was current a year or two ago. It should be borne in mind, however, that these numbers represent aggregates of filaments. If we consider the actual unit filament, the artificial silks are produced at an average range of 5 to 8 deniers, which is about twice the weight of the true silk as spun by the silkworm.

In the production and applications of cellulose acetates there has been a noteworthy advance. There are now three centres of this manufacture, in the hands respectively of 'Fürst v. Donnersmarck Kunstseide und Acetatwerke,' the well-known manufacturing corporation 'Farbwerke vormals F. Bayer & Co.,' and A. D. Little, of Boston, Mass., with his associates Walker and Mork. One of the most important uses of these products is in insulating fine copper wire of dimensions 0·07 mm. to 0·17 mm., by applying a coating of the acetate of about 0·02 mm. thickness. This wire has not only high insulating capacity, but an extremely low specific induction, and is being extensively used in the electrical industries. Other important applications of this group of esters are awaiting the necessary reduction in cost of production.

Applications of Viscose.

We have already spoken of the conversion of 'viscose' into a lustracellulose or 'artificial silk,' but this is only a particular effect.

The applications of the cellulose sulphocarbonate, in fact, are many sided. They are necessarily fraught with the obvious difficulties determined by the characteristics of these compounds. *Ils ont les défauts de leurs qualités.* To this cause must be ascribed the tardy development of the special industrial effects and products which are based upon the applications of 'viscose.' It is important to take these in brief review, not only on account of the special technical effects, but as a document illustrating some conditions of technical progress which are not generally taken into account.

The following products are now manufactured in increasing quantity:

PAPER AND BOARDS from pulps sized with viscose in the engine. Various particular effects are compassed of which the more important are: high strength and stretch, resistance to water, surface finish, generally the appreciation of raw materials with less preparation (beating). Incidentally should be noted the colour-fixing function of the regenerated cellulose; a large number of 'engine' colourings are very much faster to light in the case of viscose-sized papers.

The surface and 'body' sizing of papers by means of viscose produces a number of effects which may be deduced from the quite exceptional properties of cellulose as a plastic colloid, the structural properties of which are uniformly continuous. But the special results obtainable have only been industrially developed in one direction. This application, however, involves the general technical principle of 'appreciation.' It is evident that a paper sized with 'viscose'—

i.e. indurated with the regenerated cellulose—is able to resist the action of water and boiling solutions, and it can therefore be dyed, printed, and otherwise handled as a textile fabric. This is at once a considerable extension of technical practice and method, and a widening of the province of application of papers. Papers treated in this way, dyed in the ordinary 'jigger' machine, printed by calico-printing methods, embossed and otherwise 'finished' by the method applied to textile cloths, are now produced on the industrial scale and will in due time take their place as articles of general usefulness.

APPLICATIONS TO TEXTILES.—The uses of viscose in the dyeing, printing, and finishing of cellulose textiles have been very slowly developed. Certain special effects were early recognised as producible by means of this product—e.g. fast pigment prints upon calico, lustre finishes on cotton goods, and 'shrunk' finishes on unbleached flax and hemp goods—and these have been steadily developed. More recently special attention has been given to black lustre finishes which are now industrially worked. But the most interesting and important applications are those which are more obviously conditioned by the special properties of cellulose, in which the proportions used—i.e. added—are sufficiently large to give particular effect to them, of which we may mention:

1. *Finishes upon cloth* in which the cellulose takes the form of a continuous film. Such 'finishes' are applicable as *book cloths*, *window-blind cloths*. They are characterised necessarily by a considerable addition of substance and weight, —e.g. 20 to 50 p.ct.—and the added substance being a true 'cellulose' constitutes an obvious superiority to starch, gelatin, and other filling agents previously employed.

2. *Textile yarns*, chiefly cotton and flax, are coated with viscose, which is applied and coagulated *in sitû* by a special mechanical process, afterwards fixed, and the yarn finished and

dried, so as to conserve the lustre tenacity and elasticity of the structureless cellulose. The addition of cellulose is carried to three times the weight of the original textile, and with these large proportions the original yarn is so entirely enveloped, that its presence can only be recognised on close examination. The products have somewhat the appearance of a horsehair, but of regular dimensions and of continuous length ; they are, however, more lustrous, and the effects obtained in the goods woven with them may be described as an unusual combination of firmness to rigidity with a certain softness of touch and a silky lustre. These products are now making rapid headway on the Continent, in the hands of the exclusive licencees under the respective patents—in France, the Société Française de la Viscose, who were the originators of these developments ; in Germany, the Fürst v. Donnersmarck Kunstseide und Acetatwerke.

Cellulose Films.—In the effects above described, the added cellulose constitutes a film or visibly continuous mass. Many and exceptional difficulties have stood in the way of preparing the cellulose—regenerated from viscose—as a film, in continuous length and large dimensions, without the support of a textile fabric. But the pure cellulose, in the form of a transparent film, is now industrially produced (*a*) as a tube for use as a dialysing septum, and (*b*) a capsule for sealing bottles containing 'chemical,' pharmaceutical, and dietetic preparations.

The former have been adopted after lengthened experimental trials at such important centres of work and investigation as the Pasteur Institute No publication has been made of the results obtained with these tubes as a contribution to the theory and practice of osmotic separations. We can therefore only reproduce the statement in general terms of the particular efficiency of cellulose (hydrate) as a homogeneous

membrane. It has obvious specific advantages in many cases as a non-nitrogeneous medium, and through being particularly resistant to the actions of alkalies. It has advantages over parchmentised cellulose, not only from the fact of its uniformity of composition, but the certain absence of 'pin-holes'—in short, by reason of its structural perfection.

The use of viscose-cellulose capsules is an interesting application of properties which in other directions constitute the particular impediment barring its employment. The viscose being applied to the surface of a cylinder with rounded end, or tube, is 'precipitated' *in sitû* and 'fixed,' and is then a tube of hydrated cellulose which is detached and washed. On exposure to the air the hydrate parts with its water, and as water of hydration constitutes 85 p.ct. of the original mass, the resultant shrinkage is correspondingly large. In shrinking upon any surface such as the neck of a bottle, the cellulose attaches itself automatically at all possible points of contact and constitutes a complete seal.

Cellulose in Massive Forms; Viscoid and Viscoid Agglomerates.—Viscose by its spontaneous reversion to 'cellulose' forms masses of hydrated cellulose of the exact dimensions of any containing vessel; the process of shrinkage then continues, and under conditions which maintain a uniform process of dehydration the cellulose becomes a uniformly compacted mass of extraordinary hardness. In the preparation of industrial products the dehydration is necessarily preceded by an exhaustive process of washing to remove the by-products of the interaction of the alkali and sulphur residues. The cellulose may also be dyed or coloured, and an indefinitely varied range of effects are then produced. These have been specially developed in the hands of the Société Française, and the Viscolith which they produce is an ornamental structural product having a number of special applications.

In admixture with various waste products, organic and inorganic, vicose constitutes an agglomerating or compacting medium, and a number of artifical structural solids may be produced. A black agglomerate composed of cellulose, china clay, or other moist filling material, with pitch and similar dense hydrocarbons, is prepared by milling the viscose with these ingredients, forming the plastic mass into cylinders or cubes, 'setting,' washing, and dehydrating the washed solid. The product is used in the engineering and electrical industries, and is know as 'viscoid.'

VISCOSE AND INDIARUBBER.—Viscose, as indicated above, can be milled with hydrocarbons to a species of permanent emulsion; and this property is taken advantage of in the production of a number of new technical effects in the indiarubber industry. The admixture of the cellulose with this group of hydrocarbons is effected in various ways, and the products differ from the 'viscoid' described in the preceding section, chiefly in the added process and effect of vulcanisation. The cellulose is similarly used in producing filmed effects (waterproofing) and in the solid agglomerates known as 'mechanicals.'

This outline of the many applications to which these derivatives of cellulose are adapted is to be taken as an illustration of practical results deducible from the properties of cellulose. In these applications only those effects are evident which belong to cellulose as a typical colloid. But in the intermediate, soluble, and plastic stage, the special chemistry of cellulose is brought into evidence. The complications attending the introduction of alkali and sulphur residues are very serious; and further difficulties result from the inherent tendencies of the products to spontaneous decomposition. The control of a complex equilibrium to which so many

factors contribute is a task which imposes very methodical and exact working. It is not to be expected, therefore, that manufacturers will devote their resources to the solution of the problems of practical working unless impressed with the conviction of certain success, and the value of the results when success is attained. We are of opinion that the applications of viscose are only a special case of the general difficulty of manipulating colloids in the absence of a general theory of the colloidal state, and the advantage of a theory or a working hypothesis is that it aids in fixing those convictions which precede successful enterprises. The industrial applications of the colloids have, it is true, been largely developed on a purely empirical basis. We look forward to considerable expansion of these industries with the adoption of a general theory.[1]

A general survey of cellulose technology produces the impression, as we have often had occasion to remark, of a high state of development of these arts, marked by extraordinary refinement of method and an accumulation of exact knowledge which, however, would scarcely rank as 'exact' by comparison with other branches of the science, or in the usual sense of the term as applied to scientific knowledge. We think this arises from the want of a theory, or generalisation applicable to the cellulose groups, as to compounds in being—i.e. in action and reaction. It is not necessary in dealing with the carbon compounds generally to separate this, the phase of actuality, from the questions belonging to their synthesis and decompositions. To put this point shortly, a vast majority of the carbon compounds may be accounted for in terms of their

[1] An important publication giving an exhaustive review of progress in this field is: *Die Viskose*, B. M. Margosches, Leipzig, 1906 (Klepzig), a brochure of 130 pages and supplement dealing with bibliography and patent literature.

past and future—i.e. their origin and decomposition—without reference to their present condition. So we may endeavour to form a mental picture of cellulose by studying its products of final proximate resolution, and as we cannot study the synthetic process under which the constituent groups are put together, we draw on our imagination, with the assistance of numerous analogies, and, assuming that they are linked by the simplest constitutional bonds, we postulate the molecular aggregate, and admit a doubt only as to the exact form of this linking, and the dimensions of the molecular unit which results.

Now we have endeavoured to show in our *exposé* of recent researches and contributions to the science of the subject that this method of dealing with 'cellulose' as a problem in constitution, when the colloidal state is introduced as a factor, necessarily breaks down. All we know of the products of resolution, and of the ultimate reacting groups of cellulose, tells us nothing of its origin and of the conditions under which it is synthesised, and throws only a partial light on its actual internal conditions as a body in being. We have endeavoured to indicate the directions of evolution of more and more comprehensive formulæ; and have also suggested that the value of a working hypothesis will be measured by its providing new directions of attack. It will aid to establish this new position of critical study if we indicate some of the avenues of investigation through which it may be applied to technological problems. We select a few typical cases:

Paper-making.—The process of beating or wet-milling of paper pulps is usually regarded as a 'mechanical' treatment: a comminution by reduction of the fibres to the necessary condition of division. But on our present view it is the milling together of two solutions. These do not develop opposing surface tensions, though the cellulose exhibits a

certain resistance to penetration by water. In recent years attention has been devoted to the effects of prolonged beating, the striking result of which treatment is to bring the cellulose to the condition of a colloidal solution; so much so that the cellulose possesses the essential physical characteristics which it manifests in solutions obtained by chemical means. The differences are those of degree. The investigation of the process of hydration becomes a problem in 'surface energy.' It may involve the question of a difference of potential between the cellulose and the water. It will certainly be effected by the presence of electrolytes, and probably favourably influenced by amphoteric electrolytes.

The ordinary processes of beating for the preparation of pulp for the paper machine range in duration from 20 minutes to 14 hours, and although not directly aimed to compass these effects of colloidal hydration, they and their attendant phenomena are of course involved and should be specifically studied.

The complex effects produced in the process of 'engine sizing,' which are usually referred to the extrinsic effects of the added sizing agents, rosin (soaps), starch, sulphate of alumina, obviously involve a web of colloidal interactions, and it cannot be a matter of indifference to the technologist as to how these interactions succeed one another, and what is the ultimate balance of effect or equilibrium. To investigate and control these interactions we need to apply the methods and theories which are contributing to the rapid advance of our knowledge of the colloidal state.

Textile Bleaching and Finishing.—The chemical processes employed in preparing the cellulose textiles for their ultimate marketable condition are usually regarded merely as methods of eliminating 'impurities,' coloured and otherwise. But it is obvious that the cellulose itself is modified in interior

constitution by every treatment to which it is subjected. These modifications are, for the most part, entirely disregarded; in fact, for purely textile uses the tests applied are entirely external in significance. It is true, however, that certain directions of employment impose conditions which involve altogether different factors, and these have made technologists aware of a wide range of variations in celluloses, which would rank as of an invariable standard if judged from the standpoint of structure and external appearance. We may instance more especially the celluloses required for the preparation of nitrates, acetates, sulphocarbonates, and the aqueous solutions of cellulose. In these directions of employment the interior constitutional factors manifest their influence. Not only is the course of the reactions of synthesis effected, but the physical properties of the final product. As a single illustration we may take two samples of cotton, one of which has been 'modified' by the process of mercerisation, and expose them to esterifying conditions, for the production of nitrate or acetate. In the one case we obtain no reaction, or only such degree of reaction as indicated by a gain of weight of 6 to 10 p.ct., whereas the original cotton under the same conditions gives a maximum reaction with a gain of weight of 70 to 80 p.ct.

The technology of the nitrates of cellulose, while it imposes a very exact study of the raw materials employed, has not contributed to the scientific co-ordination of these facts, as might have been expected, probably from the reason that the knowledge is withheld from publication. In any case, however, the basis of this knowledge is empirical, so far as it is accumulated without the direction of a working hypothesis as to the constitution of cellulose. This hypothesis we have now suggested; it will be found to open up a number of lines of investigation which, as they have already been found to be

fruitful, will no doubt contribute to more general progress in this branch of technology.

But if these synthetical reactions of cellulose are affected by the antecedent conditions of its preparation, reciprocally, these reactions can be employed as a means, certainly the most important means, of diagnosing the changes determined by the processes employed by the bleacher. This opens a wide field for investigation, together with the prospect of co-ordinating the unclassified experiences of technologists in this branch with a general theory of cellulose constitution.

The operations of 'finishing,' which also appear to be hedged round with a great deal of the 'secrecy' which appertains to the 'fine art' sections of the cellulose industries, are capable of many explanations deducible from the general views herein expounded. Every operation through which a cloth passes leaves its impress on the constitution of the cellulose, and therefore on the factors which determine structural qualities, and even such external features as 'surface' and 'lustre' and feel. The essential factors of finishes are, therefore, the actual constitution of the cellulose unit; and the modifications determined by added 'conditioning' agents are of secondary importance.

The relation of 'finishing' quality to the bleaching processes employed becomes, on this view, a definite object of investigation. Probably it will be found that the most immediate criteria of the condition of a bleached textile is its relation to atmospheric moisture and its specific affinities to typical dyestuffs. Underlying these relationships are the more fundamental conditions of constitution, which can only be brought to light by applying the test of a synthetical reaction. In any case, from our present point of view it is not satisfactory to judge the quality of a 'bleach' merely on the external evidence of colour and textile quality. Progress

must result from an exercise of our grasp of the unseen and underlying causes of quality.

Dyeing and Printing.—What we have indicated above is already in part recognised in relation to the routine practice of dyeing and printing. As an instance, a 'printer's bleach' of cotton, cloth, or calico is a different effect from that which fulfils the standard of a 'market bleach,' and is tested by a special dyeing test in an alizarin bath, followed by soaping. The 'purity' of the 'bleach' is inversely as the depth of tint communicated to the cellulose. This is an empirical test, but one which, in correlation with others such as we have indicated, may be made to furnish much fuller information as to the actual condition of the cellulose. But it is in relation to dyeing phenomena that we have been able to show the gradual recognition of the amphoteric activity of cellulose; more than that, that as a typical colloid its behaviour with colouring matters depends in the first instance upon coagulation by interactions of ions of electrically opposite function, ions of the colouring matter and ions of the fibre colloid. This proceeds from a positive consistent theory, or at least a working hypothesis, in which are merged and generalised the older partial theories represented by such terms as 'mechanical' and 'chemical' applied to particular modes of explaining these phenomena.

We are still of opinion that there has been a disparity of the attention of investigators in regard to the two sides of dyeing phenomena; the fibre colloids have been relatively little studied. With a general hypothesis as to their constitution in the form of a positive connecting-link with the modern developments of the 'theory of solution,' the way is opened for definite experimental issues to be put and solved.

Artificial forms of Cellulose and Cellulose Derivatives.—It is necessarily to this branch of technology, which includes

the industries in artificial silk (lustracellulose), monofil fibres and solid agglomerates, that we look for the most important contributions to the general theory of the solid state, and to the particular problems of cellulose constitution.

It will be appeciated that the industrial process of converting the fibrous celluloses into 'artificial silk' involves an extraordinary refinement in the adjustment of factors of essentially variable character, and many of these variables are intimately connected with the constitution of the cellulose employed. It is equally evident that these industries have been perfected upon a vast accumulation of the results of exact experiments, which are scientific documents of considerable prospective value when applied in connection with general theories; both in verification of these theories and by reciprocal contribution of new matter for the extension of these theories. Thus these processes give us control of the plastic forms of the celluloses and derivatives, and we can produce them in regular continuous form, or solid aggregates of any desired dimensions. This brings a number of the physical and mechanical properties of the celluloses within the scope of exact measurement, seeing that the factors of surface and volume can be determined within the limits of ascertainable error. As we have frequently pointed out, these physical properties are specifically connected with chemical constitution, and the study of these relations is much facilitated by the control of factors which vary so irregularly in the 'natural' forms of cellulose as to make exact determinations impossible.

It is not the purpose of this essay to formulate the many objectives of research in terms, nor to anticipate the results of such research. Our aim is to provoke discussion and generally to indicate directions of investigation, which we hope will be undertaken without regard to 'specialist's' qualifications.

ADDITIONAL BIBLIOGRAPHICAL NOTES

We briefly notice certain publications which have important bearings, direct or indirect, upon the subject-matter of this volume, without however contributing to the immediate elucidation of the special points discussed.

OBSERVATIONS ON COTTON AND NITRATED COTTON.

H. de Mosenthal (J. Soc. Chem. Ind. 1904, 23).

Contains the results of laborious observations of the minute structure of the cotton fibre and of the derivative esters, with an examination of the characteristics of their solutions, including observations on the dialysis of solutions of the nitrates.

The author's methods and results, when extended and developed, will be a valuable contribution to the solution of the problem of the relation of visible structure to the constitution of the aggregate or reacting unit.

THE SURFACE STRUCTURE OF SOLIDS.

G. T. Beilby, Third Hurter Memorial Lecture (J. Soc. Chem. Ind. 1903).

This is a contribution to the general problem of solid structures, but specially directed to the condition of matter in

metallic masses, the surfaces of which are composed of films, with a proportion of spicular masses of minute dimensions which have characteristics sufficiently invariable to be regarded as structural components. The film-matrix is the evidence of the tendency to surface-flow under the action of pressure, which the author has observed to occur not only in metals but in the widest range of solid bodies examined, 'glass, agate . . . salts of all kinds . . . gelatin and cellulose.'

C.B.S. UNITS AND STANDARD PAPER-TESTS: AN ESSAY TOWARDS ESTABLISHING A NORMAL SYSTEM OF PAPER-TESTING.

C. F. Cross, E. J. Bevan, Clayton Beadle, and R. W. Sindall (London, 1903, Wood Pulp, Ltd.).

This is a symposium, the purpose of which is sufficientl explained by the title. It is pointed out that the standard adopted in Germany and on the Continent, with their obviou advantages, are defective in important respects. The con ventional standard of 'breaking length' introduces certai errors which in the case of loaded papers may be very large and which are to the advantage of the buyer as against th paper-maker. The authors point out that the numerica records of use to the paper-maker in controlling his manu facture are those which set out the physical characteristics o papers in the simplest terms, and they give particular pro minence to measurement of air-space (as a measure of 'bulk') breaking-strain (*a*) per unit of total sectional area; (*b*) pe unit of area of fibrous components ('specific tenacity').

BIBLIOGRAPHIE DER KOLLOIDE.

ARTHUR MÜLLER (Leipzig, 1904, L. Voss).

This bibliographic *résumé* of investigations of colloids and the colloidal state is of particular value at the present juncture, when the subject is attracting attention in so many directions. The author notices more than 350 original publications, and covers a much more extensive range than that comprised in the 'Index to the Literature of Colloids' of Whitney and Ober (J. Amer. Chem. Soc. 1901, 23, 856-63).

It is perhaps of interest to note that 'cellulose' is conspicuous by its absence from the extensive range of subjects and objects investigated.

PAPIERSTOFFGARNE: IHRE HERSTELLUNG, EIGENSCHAFTEN UND VERWENDBARKEIT.

By E. PFUHL (Riga, 1904, G. Löffler).

This is an important monograph of the new industrial developments based on the wet-spinning of short fibres. Paper-makers' 'pulps' are reduced in the beating engine, run on a paper machine into strips in continuous lengths, which are afterwards subjected to a twisting operation and converted into yarns available for weaving. Two or three systems are now commercially developed and the industry is of growing importance. The author treats fully of this aspect of the matter, while devoting considerable attention to the technical characteristics of the products. It is an interesting contribution to the general question of the structure of fibrous aggregates and their derived physical or mechanical properties.

The work comprises one hundred and fifty pages, with

ON THE ACTION OF WOOD ON A PHOTOGRAPHIC PLATE IN THE DARK.

W. J. RUSSELL (Phil. Trans. B. 1904, 197, 281).

This is a further contribution of experimental observations of the curious chemical activity of wood surfaces, brought to demonstration by actions on sensitised plates in the dark. These actions are influenced by previous insolation of the objects. Exposure to light also renders active various resins, turpentine, and varnishes. These observations are of considerable prospective interest, but in the absence of any positive conclusions of the author as to the actual cause of these effects, we can only note them as an index of an active condition of lignocellulose surfaces.

CELLULOSE, CELLULOSEPRODUKTE UND KAUTSCHUKSURROGATE.

JOSEPH BERSCH (Leipsig, 1904, A. Hartleben).

Authorised English translation of the above, by W. T. Braunt, published under the title, 'Cellulose, Cellulose Products, and Artificial Rubber,' London, 1904, Kegan Paul, Trench, Trübner & Co.

The scope of this work is in the main 'technical'; it aims to give a full account of the more recently developed cellulose industries. The following heads of chapters will give a general idea of the work: (1) 'Cellulose,' a general sketch of the chemistry of cellulose; (2) Wood pulp ('mechanical'); (3) Wood pulp ('chemical'); (4) Vegetable parchment; (5) Manufacture of sugar and alcohol from wood and wood cellulose; (6) Manufacture of oxalic acid from wood; (7) Viscose and viscoid; (8) Nitrocellulose (gun-cotton, pyroxylin); (9) Artificial silk; (10) Artificial cellulose fibres;

11) Viscose-spinning; (12) Celluloid; (13–14) Indiarubber substitutes.

The matter is comprised in four hundred pages, with a full index.

VISCOSE: PREPARATION, PROPERTIES, AND APPLICATIONS, WITH SPECIAL REFERENCE TO ITS USES IN THE TEXTILE INDUSTRIES.

B. M. MARGOSCHES (Leipzig, 1906, A. Klepzig).

Die Viskose—ihre Herstellung, Eigenschaften und Anwendung.

This is an exhaustive account of the technology of the cellulose xanthogenic acids, the descriptive portion occupying a hundred and thirty pages of matter, and a bibliography of the subject forming an appendix of eighty-seven additional pages. The substance of the work appeared in a series of articles in the Zeitschrift f. d. Gesamte Textil-Industrie, during the period 1904–06. The information contained in this work is not only extensive, but—what is by no means always to be said of works of this character—correct.

The encyclopædic character of the book conforms with its obvious purpose and scope, and precludes a more extensive notice. It will be recognised as a valuable addition to the literature of 'cellulose,' and indispensable to those who are interested in technological developments.

CHAPTERS ON PAPER-MAKING.

CLAYTON BEADLE (Vol. I. 1904; Vol. II. 1906; H. H. Grattan, London).

The first of these volumes reproduces a series of ten lectures delivered by the author on behalf of the Battersea Polytechnic Institute, and traverses a number of subjects of

special interest to paper-makers desirous of following up the scientific technology of the manufacture, including 'Raw Materials,' 'Bleaching,' 'Physical Properties of Papers and Paper-testing,' 'Chemical Residues in Papers.'

The treatment of these subjects is original, and the author embodies the results of several of his own experimental investigations. The second volume is more 'educational' in its purpose and scope, and the author has devoted himself to a full consideration of the examination papers of the City and Guilds Institute, on the subject of paper-making, during the period 1901–05.

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